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ATMOSPHERIC MEASUREMENTS OF SELECTED TOXIC ORGANIC CHEMICALS

Interim Report - 1979

by

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Atmospheric concentrations of 37 selected toxic organic chemicals, including aromatic hydrocarbons, halohydrocarbons, and secondary organic pollutants were measured under varying meteorological and source-strength conditions at several urban locations - Los Angeles, California; Phoenix, Arizona; and Oakland, California. Ambient air measurements of these chemicals were conducted from a suitably equipped mobile laboratory using specifically developed analytical techniques. Preliminary results on concentrations and variability, average daily exposure dosage, diurnal behavior, and atmospheric distribution, abundance, and fate are presented.

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ABSTRACT

The first year research effort for this project consisted of a program of development of analytical methods for the accurate ambient analysis of a large set of organic toxic chemicals, field data collection and analysis, and interpretation of collected data. During field data collection, in-situ analysis using an instrumented mobile laboratory was performed for a total of 37 chemical species, including haloethanes, halomethanes, chlorinated ethylenes, chlorinated aromatics, aromatic hydrocarbons, and secondary organics ($COCl_2$, PAN, and PPN). Six important meteorological parameters were also measured. Three field studies, each of roughly two-weeks duration, were successfully conducted in Los Angeles, California; Phoenix, Arizona, and Oakland, California. A round-the-clock measurement schedule (24 hours per day) was followed at all three sites, permitting extensive data collection.

The concentrations and variabilities of all measured pollutants and average daily dosages from exposure to these pollutants were determined. The diurnal behavior and the atmospheric fate of both primary and secondary pollutants were studied. Residence times for a typical polluted atmosphere were estimated. The atmospheric distributions and abundances of many species have been defined for the first time. Average daily-dose levels of all three sites for exposure to halomethanes (excluding fluorocarbons), haloethanes, chloroethylenes, chloroaromatics, aromatic hydrocarbons, and secondary organics were determined to be 298, 142, 203, 53, 1880, and 257 μg/day, respectively. Exposure levels in Los Angeles were typically the highest and those in Oakland the lowest.

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SECTION 1
INTRODUCTION

A vast number of potentially harmful organic chemicals are released into the environment, and it is becoming increasingly apparent that these chemicals contribute to the growing rate of cancer in industrialized countries. Despite recent and intense interest in toxic chemicals, the atmospheric abundance and fate of this important group of pollutants remains poorly understood. The purpose of this study project is to characterize the concentrations of a wide range of toxic organic chemicals at several urban and source-specific locations under varying meteorological and source-strength conditions. The measurement of these toxic chemicals is being conducted by in-situ analysis of ambient air using a suitably outfitted mobile laboratory. The overall program of analytical methods development, field measurements, data collection, and analysis is expected to provide information that will permit determination of the atmospheric abundance and chemistry of this potentially harmful group of chemicals.

The research plan is primarily designed to answer the following basic questions:

- What are the concentration levels and variabilities of selected toxic organic chemicals in typical urban environments?
- What are the atmospheric fates of these chemicals?
- What is the extent of human exposure to selected toxic chemicals?

The answers to these questions will be sought through a combination of approaches:

- A comprehensive program of field measurements at several urban locations and near several source-specific locations.
- Analysis of data collected during the field measurements and integration of this information with data acquired from outside sources.
- Compilation of all available information dealing with the sources, sinks, chemistry, and effects (health as well as environmental) of the toxic chemicals of interest.

This summary report presents the results accomplished during the first year of a three-year research effort. Analysis of data collected during the first year is by no means complete: Additional analysis will be presented in forthcoming reports and publications.

SECTION 2
OVERALL OBJECTIVES

The overall objectives of the proposed study are to:

- Characterize the abundance and variabilities of selected toxic organic chemicals in urban environments.
- Investigate and assess the atmospheric fates (sources and sinks) of these toxic chemicals.
- Determine the extent of human exposure.

To achieve these objectives, SRI will use the following approach:

- Develop and standardize new and improved procedures for sampling and analyzing toxic chemicals.
- Measure the atmospheric concentrations of toxic chemicals at several representative locations to develop a valid data base for ambient levels of toxic chemicals, and use these measurements to better understand the atmospheric fates of these chemicals.
- Update, validate, and assimilate information of production, emissions, atmospheric abundance, fates, and effects of toxic chemicals based on a continued program of literature search and information gathering.
- Develop and synthesize information on sources, removal mechanisms, extent of exposure, and health effects suggested by the preceding tasks.

SECTION 3

SUMMARY AND CONCLUSIONS

The first year research effort involved a program of analytical methods development, field data collection and analysis, and interpretation of collected data. One of the most advantageous features of this research effort was SRI's ability to conduct in-situ ambient measurements with the help of an instrumented mobile laboratory. After completion of a program of methods development, three studies, each of roughly two-weeks duration, were conducted in Los Angeles, California (Site 1); Phoenix, Arizona (Site 2); and Oakland, California (Site 3). In all cases a round-the-clock measurement schedule (24 hours per day) was followed, permitting the collection of a large amount of data. A total of 37 chemical species and 5 meteorological parameters were measured. Thirty-three of the measured chemicals were organics that are either known or have the potential to be toxic: Over a dozen are suspected carcinogens.

Table 1 summarizes the average concentrations measured at each of the sites and the daily average exposure based on a total air intake of 23 m^3/day for a 70 kg male. The corresponding standard deviations associated with these parameters are also shown in Table 1. Table 2 summarizes average exposures (μg/day) to individual categories of chemical groups at each of the sites. Overall, the total exposure to measured toxic chemicals at Site 1 is more than four times that measured at Site 3. As a category, exposure to aromatic hydrocarbons is the highest and that to chloro aromatics lowest. Daily outdoor exposure to measured toxic species is determined to be 4442, 3041, and 1037 μg/day at Sites 1, 2, and 3 respectively.

In order to assess the atmospheric fates of measured toxic chemicals their mean diurnal variations were studied at each of the sites. In addition, the chemical residence times and daily loss rates of these pollutants were estimated. It is clear from these estimates that the fates of toxic organic chemicals differ widely; the species vary from highly reactive to essentially inert. Residence times can vary from an hour to several decades. Table 3 provides our best estimate of the residence times of measured species in a polluted atmosphere and their daily loss rate caused by chemical reactions. Diurnal behavior of each of the chemicals measured is determined and the results are discussed in the text. At Site 2 (Phoenix) an afternoon minimum almost always exists because of deep vertical mixing (hot and dry climate) and its superimposition on chemical loss. Detailed analysis of ambient data would require knowledge of source strength and its diurnal variability. Such data is currently unavailable for a majority of chemicals measured.

TABLE 1. CONCENTRATIONS AND DAILY DOSAGES OF TOXIC CHEMICALS

Chemical Group and Species	Los Angeles (Site 1)				Phoenix (Site 2)				Oakland (Site 3)			
	Concentration (ppt)		Daily Dose* (µg/day)		Concentration (ppt)		Daily Dose (µg/day)		Concentration ppt)		Daily Dose (µg/day)	
	Average	S.D.†	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.
Halomethanes												
Methyl chloride	3002	1759	140	57	2391	940	109	20	1068	781	60	48
Methyl bromide	244	194	25	13	67	47	6	2	55	24	5	1
Methylene chloride	3751	2620	309	137	893	989	86	42	416	315	33	9
Chloroform	88	40	11	3	111	106	12	4	32	12	4	1
Carbon tetrachloride	215	107	32	7	277	114	40	5	169	133	23	4
Haloethanes												
1,1 Dichloroethane	–	–	–	–	–	–	–	–	–	–	–	–
1,2 Dichloroethane	519	233	79	17	216	220	27	33	83	106	8	4
1,2 Dibromethane	33	26	6	3	40	38	7	3	16	13	3	1
1,1,1 Trichloroethane	1028	646	133	45	824	597	116	39	291	161	38	11
1,1,2 Trichloroethane	9	6	1	0	16	10	1	1	8	4	1	0
1,1,1,2 Tetrachloroethane	4	2	0	0	9	4	0	0	4	1	1	0
1,1,2,2 Tetrachloroethane	17	11	3	1	17	6	2	1	7	3	1	0
Chloroethylenes												
Vinyledene chloride	5	3	0	0	30	37	3	2	13	5	1	0
1,2 (cis) Dichloroethylene	–	–	–	–	–	–	–	–	–	–	–	–
Trichloroethylene	399	302	58	33	484	587	76	58	188	270	20	9
Tetrachloroethylene	1480	445	236	31	994	716	173	32	308	292	46	22
Chlorobenzenes												
Monochlorobenzene	200	–	21	–	200	–	21	–	100	–	10	–
o-Dichlorobenzene	125	99	19	10	226	348	28	17	40	50	5	2
m-Dichlorobenzene	77	56	11	4	87	59	11	3	65	29	8	2
1,2,4 Trichlorobenzene	69	49	12	6	31	21	5	1	30	24	6	5
Aromatic hydrocarbons												
Benzene	6040	4580	424	202	4740	6750	345	156	1550	1220	105	41
Toluene	11720	9070	1028	421	8630	9090	705	288	3110	3180	261	87
Ethyl benzene	2250	4470	213	169	2000	2870	182	78	600	670	59	29
m/p-Xylenes	4610	6140	439	217	4200	4660	419	161	1510	1420	151	51
o-Xylene	1930	1830	192	84	1780	1880	171	61	770	730	69	22
4-Ethyl toluene	1510	1450	175	79	1510	1500	170	59	660	620	66	14
1,2,4 Trimethyl benzene	1880	2380	196	112	1740	1910	201	72	–	–	–	–
1,3,5 Trimethyl benzene	380	680	34	23	400	370	31	12	–	–	–	–
Secondary organics												
Phosgene	–	–	–	–	–	–	–	–	50	5	5	1
Peroxyacetyl nitrate	4977	4483	550	277	779	767	86	27	356	422	32	13
Peroxypropionyl nitrate	722	673	77	50	93	77	6	2	149	118	16	6

*Based on average air intake of 23 m^3/day.

†Standard deviation

TABLE 2. AVERAGE DAILY EXPOSURE TO MEASURED TRACE CHEMICAL GROUPS

Chemical Category*	Total Average Daily Dose (μg/day)		
	Los Angeles (Site 1)	Phoenix (Site 2)	Oakland (Site 3)
Halomethanes	516	253	124
Haloethanes	222	153	52
Chloroethylenes	292	251	67
Chloroaromatics	63	65	30
Aromatic hydrocarbons	2700	2228	710
Secondary organics	627	91	54
Total	4420	3041	1037

*Fluorinated species such as fluorocarbons are excluded. For the constituents in each category see Table 1.

TABLE 3. ESTIMATED RESIDENCE TIMES AND DAILY CHEMICAL LOSS RATES OF SELECTED TOXIC CHEMICALS

Chemical Name	Chemical Formula	Rate Constant $10^{12} \times k_{HO}$* (300°K)	Residence Times τ_c† (days)	Percent Loss in One Day (or 12 sunlit h)
Methyl chloride	CH_3Cl	0.05	231	0.4
Methyl bromide	CH_3Br	0.04	289	0.4
Methylene chloride	CH_2Cl_2	0.15	77	1.3
Chloroform	$CHCl_3$	0.10	116	0.9
Carbon tetrachloride	CCl_4	<0.001	>11600	≈0.0
1,1 Dichloroethane	CH_3CHCl_2	0.26	44	2.3
1,2 Dichloroethane	CH_2ClCH_2Cl	0.22	53	1.9
1,2 Dibromoethane	CH_2BrCH_2Br	0.25	46	2.2
1,1,1 Trichloroethane	CH_3CCl_3	0.02	579	0.2
1,1,2 Trichloroethane	$CH_2ClCHCl_2$	0.02	579	0.2
1,1,1,2 Tetrachloroethane	CH_2ClCCl_3	<0.01	>1160	<0.1
1,1,2,2 Tetrachloroethane	$CHCl_2CHCl_2$	<0.01	>1160	<0.1
Hexachloroethane**	CCl_3CCl_3	<0.001	>11600	≈0.0
Vinyl chloride	CH_2CHCl	6.6	1.8	42.6
Vinyledene chloride	CH_2CCl_2	4.0‡	2.9	29.2
1,2 Dichloroethylene	$CHClCHCl$	4.0	2.9	29.2
Trichloroethylene	$CHClCCl_2$	2.2	5.3	17.2
Tetrachloroethylene	CCl_2CCl_2	0.17	68	1.5
Chlorobenzene	C_6H_5Cl	0.4‡	29	3.4
m-Dichlorobenzene	m-$C_6H_4Cl_2$	0.07‡	165	0.6
p-Dichlorobenzene	p-$C_6H_4Cl_2$	0.07‡	165	0.6
o-Dichlorobenzene	o-$C_6H_4Cl_2$	0.07‡	165	0.6
Trichlorobenzene	$C_6H_3Cl_3$	0.01‡	1160	<0.1
Benzene	C_6H_6	1.4	8.3	11.4
Toluene	$C_6H_5CH_3$	6.0	1.9	40.9
Ethylbenzene	$C_6H_5C_2H_5$	8.0	1.4	51.0
m-Xylene	m-$C_6H_4(CH_3)_2$	23.4	0.5	86.5
p-Xylene	p-$C_6H_4(CH_3)_2$	12.3	0.9	67.0
o-Xylene	o-$C_6H_4(CH_3)_2$	13.9	0.8	71.3
4-Ethyl toluene	4-$C_6H_4C_2H_5CH_3$	12.9	0.9	67.0
1,2,4 Trimethylbenzene	1,2,4 $C_6H_3(CH_3)_2$	33.2	0.3	96.4
1,3,5 Trimethylbenzene	1,3,5 $C_6H_3(CH_3)_2$	49.3	0.2	99.3
Phosgene	$COCl_2$	--	--	--
Peroxyacetyl nitrate	$CH_3COOONO_2$	--	0.05§	99.9
Peroxypropionyl nitrate	$CH_3CH_2COOONO_2$	--	<0.05§	99.9

*Rate constant with hydroxyl radical (HO) in units of cm^3 $molec^{-1}$ sec^{-1}

†Calculated based on an estimated average daily (24 h) HO abundance of 10^6 molec/cc; corresponds to a daytime average (≈12 h) HO concentration of 2×10^6 molec/cc.

‡Estimated from Hendry (1979)

§ Thermal degradation in the presence of NO and NO_2

**Not measured

SECTION 4
ANALYTICAL METHODOLOGY

A. *Trace Constituents of Interest*

Since the available lists of organic toxic chemical can contain hundreds of species, it was essential to reduce this list to a manageable size. The chemicals that were chosen for study in the first year of this research effort are only suspected of being hazardous; in most cases toxicity studies are either unresolved or incomplete. In some cases, where no toxicity data were available, structural considerations were used in selecting target chemicals. Our ability to satisfactorily measure a trace constituent at the expected ambient concentration was an essential requirement for inclusion in field work. Table 4 summarizes the chemicals for which actual field data was obtained. In some instances we have chosen to not report data until further confirming tests on the identity of these species are completed. Six important meteorological parameters that were continuously measured during field studies are also noted in Table 4.

B. *Field Instrumentation*

One of the primary motivations of our study was to conduct in-situ analysis of trace chemicals, to minimize the many problems that arise when samples are collected in vessels or in tubes filled with solid sorbents and analyzed after long delays. It is widely agreed that the integrity of the air samples is assured when careful in-situ analysis is performed.

All field work was therefore conducted in an in-situ mode using a suitably instrumented mobile environmental laboratory. Table 5 summarizes the equipment that was available on our mobile laboratory for the conduct of this study. This laboratory was air conditioned for temperature control and operated on a 220-V, 80-A circuit. Provision was also devised for operating on 110-V input. A 200-m electrical cord was always used to station the laboratory away from the electrical source or a power pole. The sampling manifold was all stainless steel with a variable inlet height. In all cases the sampling manifold was adjusted to be higher than nearby structures: A typical manifold inlet height was 5 m above ground. For pumping and pressuring air samples, a special stainless-steel metal bellows compression pump (Model MB 158) was always used.

C. *Experimental Procedures*

1. *Air Analysis*

For all halogenated species and organic nitrogen compounds shown in Table 4, electron-capture (ECD) gas chromatography (GC) was the primary means of analysis. The aromatic hydrocarbons and carbon monoxide (CO) were measured using flame-ionization (FID) gas chromatography. Continuous chemiluminescent instrumentation was used for the analysis of

TABLE 4. ATMOSPHERIC MEASUREMENTS OF SELECTED CHEMICALS*

Trace Constituents	
Chemical Name	Formula
Methyl chloride	CH_3Cl
Methyl bromide	CH_3Br
Methylene chloride	CH_2Cl_2
Chloroform	$CHCl_3$
Tri-chloro-monofluoro-methane (F-11)†	CCl_3F
Tri-chloro-trifluoro-ethane (F-113)†	$CClF_2CCl_2F$
Carbon tetrachloride	CCl_4
1,1 Dichloroethane‡	CH_3CHCl_2
1,2 Dichloroethane	CH_2ClCH_2Cl
1,2 Dibromoethane	CH_2BrCH_2Br
1,1,1 Trichloroethane	CH_3CCl_3
1,1,2 Trichloroethane	$CH_2ClCHCl_2$
1,1,1,2 Tetrachloroethane	$CHClCCl_3$
1,1,2,2 Tetrachloroethane	$CHCl_2CHCl_2$
Hexachloroethane	CCl_3CCl_3
Vinyledene chloride	CH_2CCl_2
1,2(cis) Dichloroethylene‡	$CHClCHCl$
Trichloroethylene	$CHClCCl_2$
Tetrachloroethylene	CCl_2CCl_2
Monochlorobenzene	C_6H_5Cl
o-Dichlorobenzene	$o\text{-}C_6H_4Cl_2$
m-Dichlorobenzene	$m\text{-}C_6H_4Cl_2$
p-Dichlorobenzene‡	$p\text{-}C_6H_4Cl_2$
1,2,4 Trichlorobenzene	C_6H_3Cl
Benzene	C_6H_6
Toluene	$C_6H_5CH_3$
Ethyl benzene	$C_6H_5C_2H_5$
m/p-Xylene	$m/p\text{-}C_6H_4(CH_3)_2$
o-Xylene	$o\text{-}C_6H_4(CH_3)_2$
4-Ethyl toluene	$4\text{-}C_6H_4C_2H_5CH_3$
1,3,5 Trimethyl benzene	$C_6H_3(CH_3)_3$
1,2,4 Trimethyl benzene	$C_6H_3(CH_3)_3$
Peroxyacetyl nitrate (PAN)	$CH_3COOONO_2$
Peroxypropionyl nitrate (PPN)	$CH_3CH_2COOONO_2$
Phosgene	$COCl_2$
Ozone	O_3
Nitrogen Oxides	NO/NO_2
Carbon monoxide	CO

*Field measurements conducted for all compounds. Meteorological parameters measured: wind speed and direction, temperature, pressure, relative humidity, solar flux.

†Not expected to be toxic but often good indicator of type of sources and degree of contamination for a given area.

‡Data not reported for 1,1 dichloroethane and 1,2(cis) dichloroethylene since further tests are required to confirm their identity. p-Dichlorobenzene was poorly quantified from an unidentified GC peak and no quantitation was possible.

TABLE 5. ENVIRONMENTAL MOBILE LABORATORY INSTRUMENTATION*

Instrument	Features	Analysis
Perkin Elmer 3920 GC1	2 ECD†, 1 dual FID‡	Trace constituents
Perkin Elmer 3920 GC2	2 ECD, 1 dual FID	Trace constituents
Perkin Elmer 3920 GC3 (capillary column GC)	2 ECD, 1 dual FID	Trace constituents
Coulometric dual EC-GC	Coulometric ECD	Halocarbons, PAN, PPN, $COCl_2$; calibration
Beckman 6800	FID	CO-CH_4-THC
Horiba AIA-24	NDIR§	CO, CO_2
Bendix 8101-B	Chemiluminescent	NO, NO_2
Monitor Labs Model 8440E	Chemiluminescent	NO and NO_2
Dasibi Model 1003 AH	Photometric principle	Ozone
AID Model 560	Chemiluminescent	Ozone
Bendix 8002	Chemiluminescent	O_3
Eppley pyranometer		Solar flux
Eppley UV radiometer		Ultraviolet radiative flux
Miscellaneous meteorological equipment		Wind speed, wind direction, temp, pressure, dew point, relative humidity
Auto Lab IV Data System (No. 1)		GC data
SP-4000 Multichannel Data System (No. 2)		GC data
Digitem Data System (No. 3)		All continuous air quality and meteorological data
Stainless-steel manifold		Sampling of HCs and halocarbons
Teflon manifold		Sampling O_3, NO, NO_x

*Note: Finnigan 3200 GC/MS available to this project at SRI

†Electron capture detector.

‡Flame ionization detector.

§Nondispersive infrared.

O_3, NO, and NO_2. Under normal operating conditions 5 GC channels were operated with ECDs and only one with FID. Although the exquisite sensitivity of the ECD would allow the determination of several species in Table 4 with a direct 5-ml injection of air, preconcentration of air samples was necessary for efficient operation. All six GC channels were equipped with stainless-steel sampling valves and could be operated either with a direct sampling loop or with a preconcentration trap. In no instance was a sample size of greater than 1 liter used: in most cases, sample volumes of 500 ml or less were satisfactory. Sample preconcentration was conducted on a 4-inches long bed of 100/120 mesh glass beads packed in a 1/16-inch diameter stainless-steel tubing maintained at liquid oxygen temperature. The glass beads could be replaced with an equivalent length of SE-30 packing (3 percent SE-30 on 100/120 mesh acid-washed chromosorb W) or glass wool with completely satisfactory results. Desorption of chemicals from the preconcentration traps was accomplished by holding the trap at boiling-water temperature and purging with carrier gas. Electrical heating of preconcentration traps was attempted but found to be unnecessary. The traps assured completely quantitative adsorption and desorption characteristics and were found to be free of any artifact problems.

Since the use of liquid oxygen is tedious at best, we attempted to preconcentrate air samples on Tenax® traps at room temperature. Considerable testing indicates that Tenax® suffers from serious artifact problems. A number of "ghost peaks" were seen, particularly on our ECD systems. In addition, we encountered serious difficulties in quantitatively absorbing and desorbing specific species that were tested. Because of the possibility of confusing artifacts (sometimes present in significant amounts) with real pollutants, we have discontinued the use of Tenax® as a column pretrap. It appears that oxygen or ozone can oxidize Tenax® monomer to produce electron absorbing oxygenated species; therefore, all preconcentrations in this study have been performed on glass beads, glass wool, or SE-30 packing surfaces.

The sampling was achieved by pressurizing a 1-liter stainless-steel canister to 32 psi. The sampling line and the prerap (maintained at 90°C) were flushed with ambient air and the canister pressure brought to 30 psi. Sampling then began. The preconcentration trap was immersed in liquid oxygen and an air volume sampled from pressure p_1 to p_2. A high-precision pressure gauge (± 0.05 psi) was used to measure the canister pressure. A typical setting was p_1 = 30.0 psi and p_2 = 20.0. Ideal gas laws were found to hold excellently at these pressures and were used to estimate sample volumes. The pressure range of 30 to 20 psi assured smooth flow through the preconcentration traps without problems of plugging. All other sampling was accomplished by using sampling loops that were flushed with all-glass syringes of 100-ml volume.

Table 6 summarizes the GC conditions for the analysis of trace constituents of interest. Because of the dominant water response of the ECD, a post-column Ascarite trap was inserted to remove water from halocarbon analysis. No water trap was used for the analysis of aromatic hydrocarbons, PAN, PPN, and phosgene.

The ECDs were maintained at 325°C, because in most cases the ECD response increased with an increase in temperature. In the case of PAN, PPN, and phosgene, the EC-GC coulometer was maintained at 30°C: For these species, the reduced temperature seemed to give the best response. The FID was also maintained at 325°C. Table 6 shows the columns that can adequately be utilized for the separation and analysis of these chemicals, as well as the recommended columns for routine analysis.

TABLE 6. ANALYTICAL CONDITIONS FOR THE ANALYSIS OF SELECTED TOXIC CHEMICALS

GC Column			Species Measured	Detector		Typical Carrier Gas Flow Rate (ml/min)	Typical Sample Size (ml)	Remarks
No.	Description	Temp. (°C)		Type	Temp. (°C)			
1	6 ft X 1/8 in, SS,* 20% SP2100, 0.1% CW 1500 on 100/120 mesh Supelcoport	45	$CHCl_3$; CH_3CCl_3; CCl_4; C_2HCl_3; $CH_2ClCHCl_2$; C_2Cl_4; CH_2ClCCl_3; $CHCl_2CHCl_2$	Electron capture	325	40	500	No water trap
2	33 ft X 1/8 in, Ni, 20% DC 200 on 80/100 mesh Supelcoport	45	CH_3Cl; CH_3Br; CH_2CCl_2	Electron capture	325	25	500	Ascarite water trap
3	6 ft X 1/8 in, SS, 10% N, N, -bis (2-cyanoethyl) Formamide on Chromosorb P (A/W)	65	C_6H_6; $C_6H_5CH_3$; m/p/o-$C_6H_4(CH_3)_2$; 4-$C_6H_4C_2H_5$; 1,3,5 $C_6H_3(CH_3)_3$; 1,2,4 $C_6H_3(CH_3)_3$	Flame ionization	325	45	500	No water trap
4	3 ft X 1/8 in, Ni, 5% SP 1200 -5% Bentone on 100/120 mesh Supelcoport	65	C_6H_5Cl; m-$C_6H_4Cl_2$; o-$C_6H_4Cl_2$; 1,2,4 $C_6H_3Cl_3$	Electron capture	325	45	750	No water trap
5	15 ft X 1/8 in, SS, 10% SP 1000 on 100/120 mesh Supelcoport	45	CH_2ClCH_2Cl	Electron capture	330	25	100	Ascarite water trap
6	10 ft X 1/8 in, SS, 0.2% CW 1500 80/100 mesh on carbopack C	45	CH_2Cl_2; CCl_3F; cis-CHClCHCl; CCl_2FCClF_2; CH_3CCl_3; CCl_4	Electron capture	330	40	10	Ascarite water trap; also used for CH_2CCl_2 measurement with preconcentration
7	10 in X 1/4 in, Teflon, 5% CW 400, on 60/80 mesh Chromosorb W(A/W)	30	PAN, PPN	Electron capture	30	60	5	No water trap
8	5 ft X 1/4 in, SS, 30% didecyl phthalate, 100/120 mesh, Chromosorb P (A/W)	30	$COCl_2$	Electron capture	30	70	5	No water trap

*Stainless steel

The identity of trace constituents was established by using the following criteria:

- Retention times on multiple GC columns
- EC thermal response
- EC ionization efficiency
- Limited GC/MS analysis.

Details of these comparisons for halocarbon species, organic nitrogen compounds, and aromatic hydrocarbons have already been published and need not be repeated here (Singh et al., 1979; Hester et al., 1979; Stephens, 1969).

Figures 1-7 provide representative chromatograms for the atmospheric analysis of selected trace species.

2. *Calibrations*

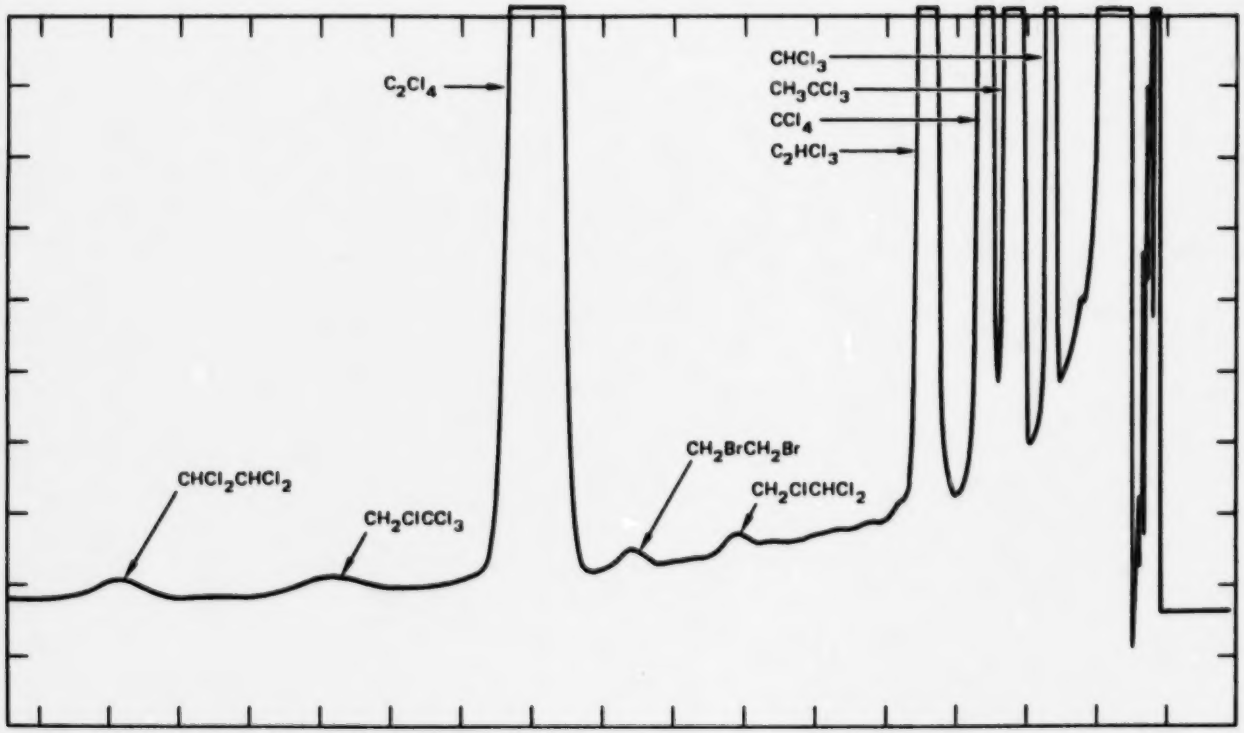
Calibrations for all toxic species of interest were performed using three basic techniques:

- Permeation tubes
- Multiple dilutions
- Gas phase coulometry.

Permeation tubes (3.2-inches long) for a large number of trace constituents of interest, constructed from standard FEP or TFE Teflon tubing of varying thicknesses, were obtained from AID Inc. (Avondale, Pennsylvania). Each permeation tube was contained in a specialized glass holder (Figure 8) which was held in a 37 liter water bath (18 × 10.5 inches) maintained at 31.0 ± 0.05°C. Permeation holders were flushed constantly with a purge gas flowing through at a rate of approximately 15 ml/min. The purge gas was prepurified helium, further passed through a sequence of traps containing charcoal, anhydrous calcium sulfate, and molecular sieve. The permeation holder inlet coil length was adequate to allow a helium flow rate 5 liters/min over the permeation (perm) tubes without causing any heat transfer problems. All tubing materials were either aluminum or glass: Fittings were either brass Swagelok or all-glass ball joints. During the generation of standards only one perm tube was used at any given time. The perm tube was flushed for about 10 min. at a preset carrier flow rate before equilibrium was established. A large-volume mixing chamber was installed at the perm tube exit to allow for complete mixing, and equilibriation syringe samples were withdrawn through a septune from the mixing chamber using all-glass syringes.

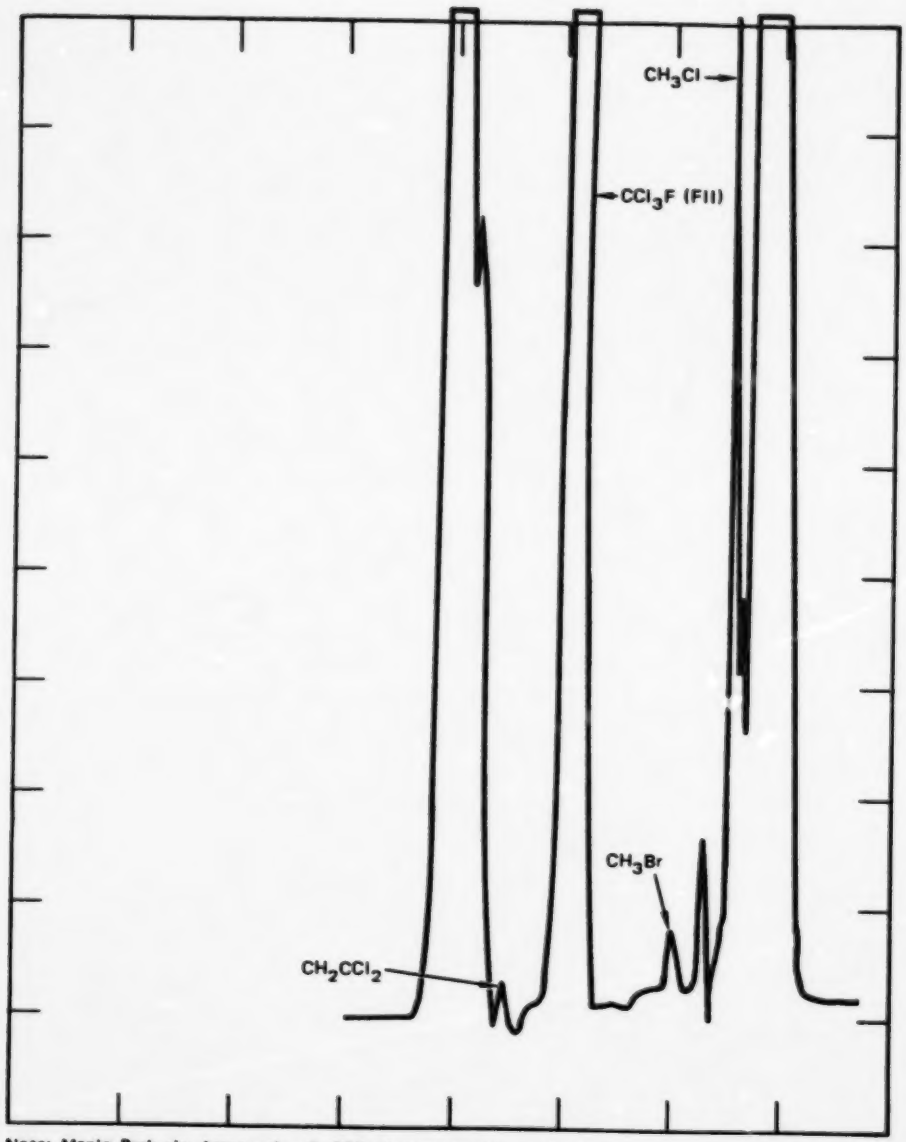
Permeation tubes were weighed at last once a week (and in many cases twice a week) on a semimicro (10^{-5}g) balance. The water bath was filled to a constant level every week with the additional water at 30-32°C to make up for the evaporation losses.

Table 7 lists the permeation rate data from the various permeation tubes tested. A number of the fluorinated species are known to be nontoxic and are not of concern in this study. However, this is the first instance that a fluorocarbon-12 permeation tube has been successfully demonstrated. The quality of the perm tube that was considered satisfactory was generally very good, and permeation rates were completely linear over a period of several months. For



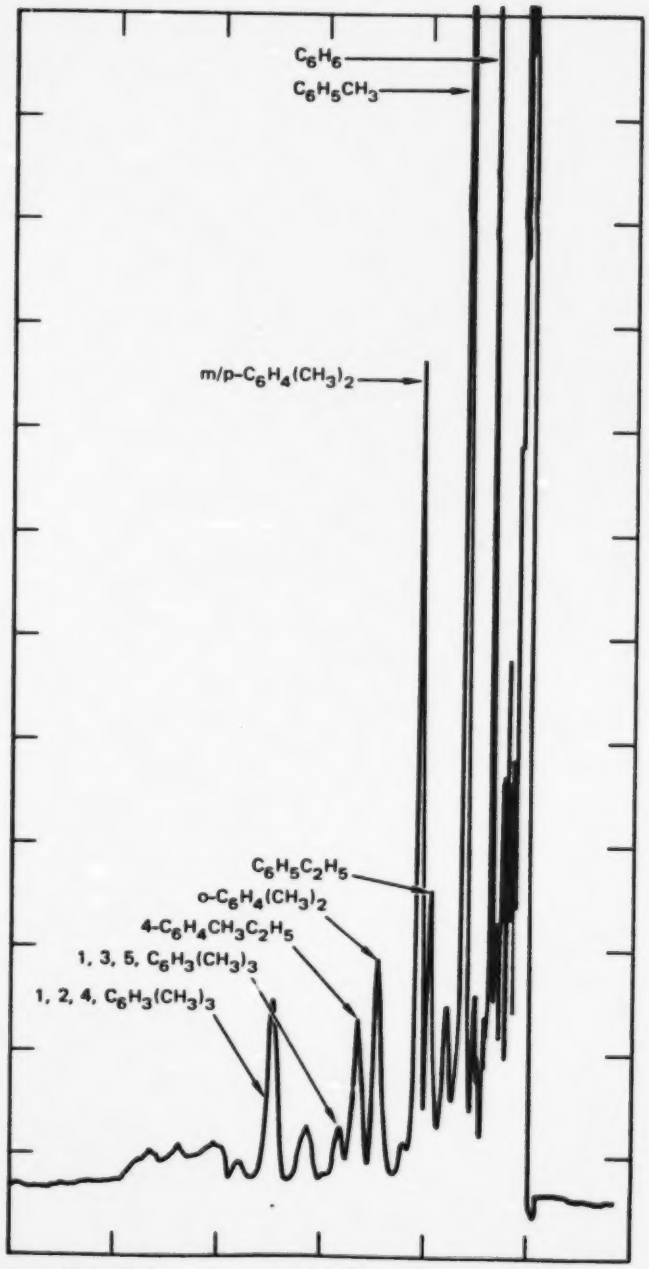
Note: Menlo Park air; Attenuation 16; 300-ml sample; Column No. 1.

Figure 1. Chromatogram showing ambient analysis of selected chlorinated and brominated toxic chemicals.



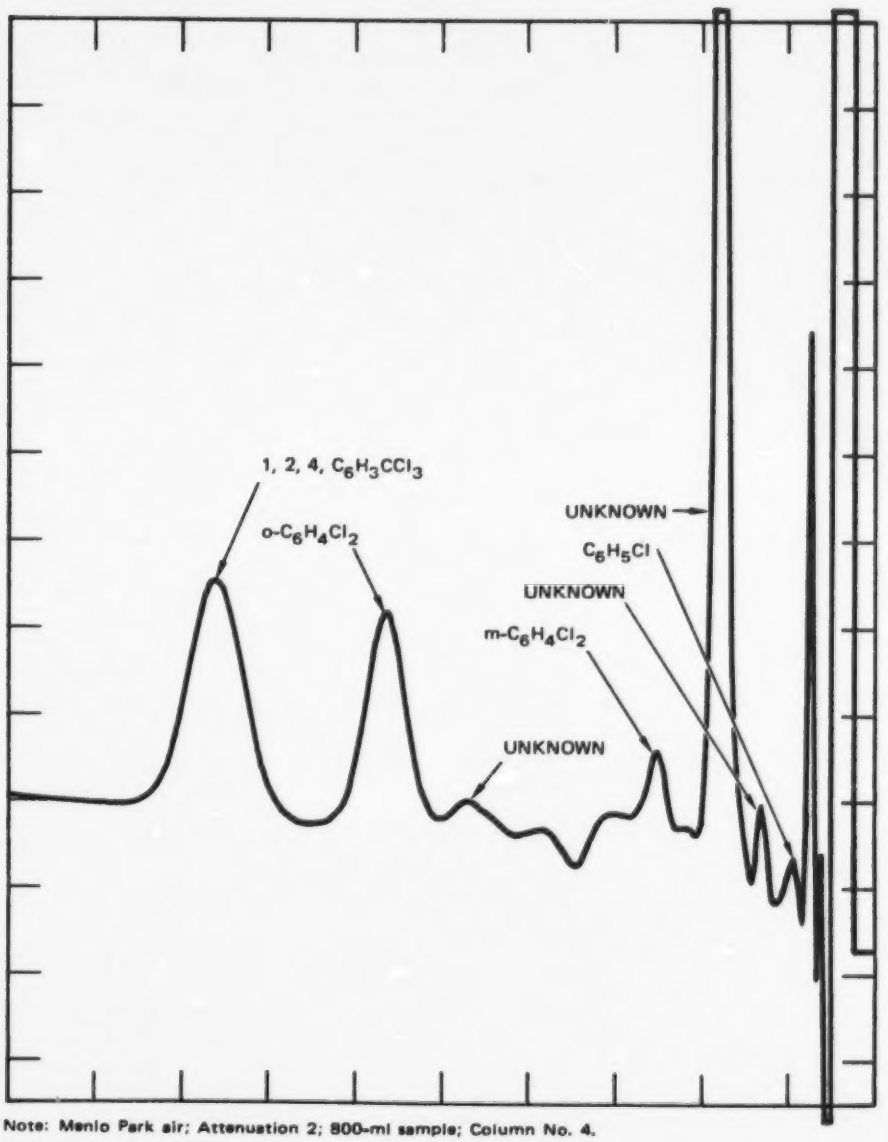
Note: Menlo Park air; Attenuation 2; 300-ml sample; Column No. 2.

Figure 2. Chromatogram showing separation of methyl chloride, methyl bromide, and vinyledene chloride from ambient air.



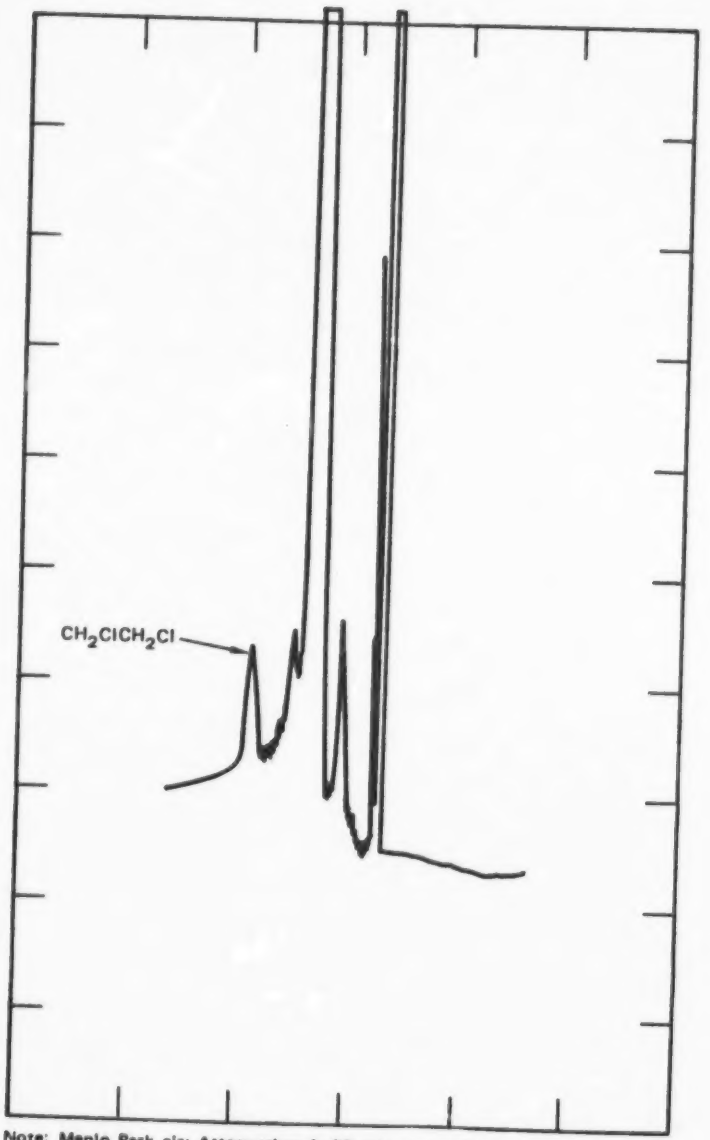
Note: Menlo Park air; Attenuation 8; 400-ml sample; Column No. 3.

Figure 3. Analysis of aromatic hydrocarbons in ambient air.



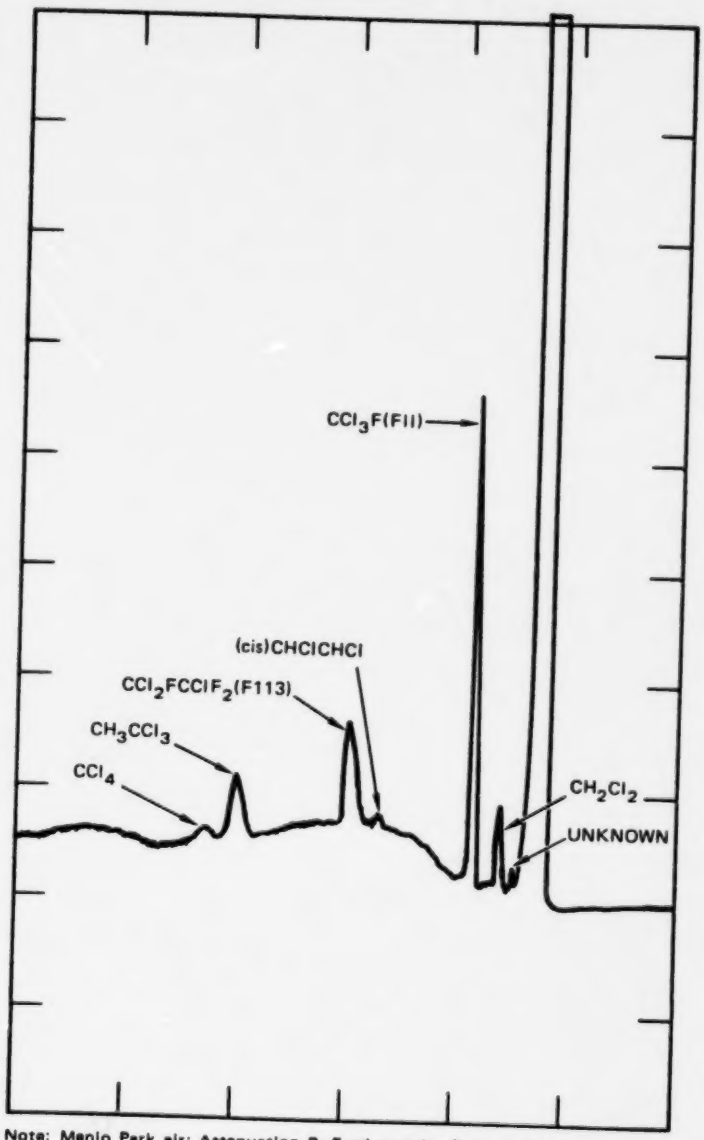
Note: Menlo Park air; Attenuation 2; 800-ml sample; Column No. 4.

Figure 4. Halogenated aromatics in the air.



Note: Menlo Park air; Attenuation 4; 50-ml sample; Column No. 5.

Figure 5. Analysis of 1,2 dichloroethane.



Note: Menlo Park air; Attenuation 8; 5-ml sample; Column No. 6.

Figure 6. Chromatogram showing methylene chloride separations from other halocarbons.

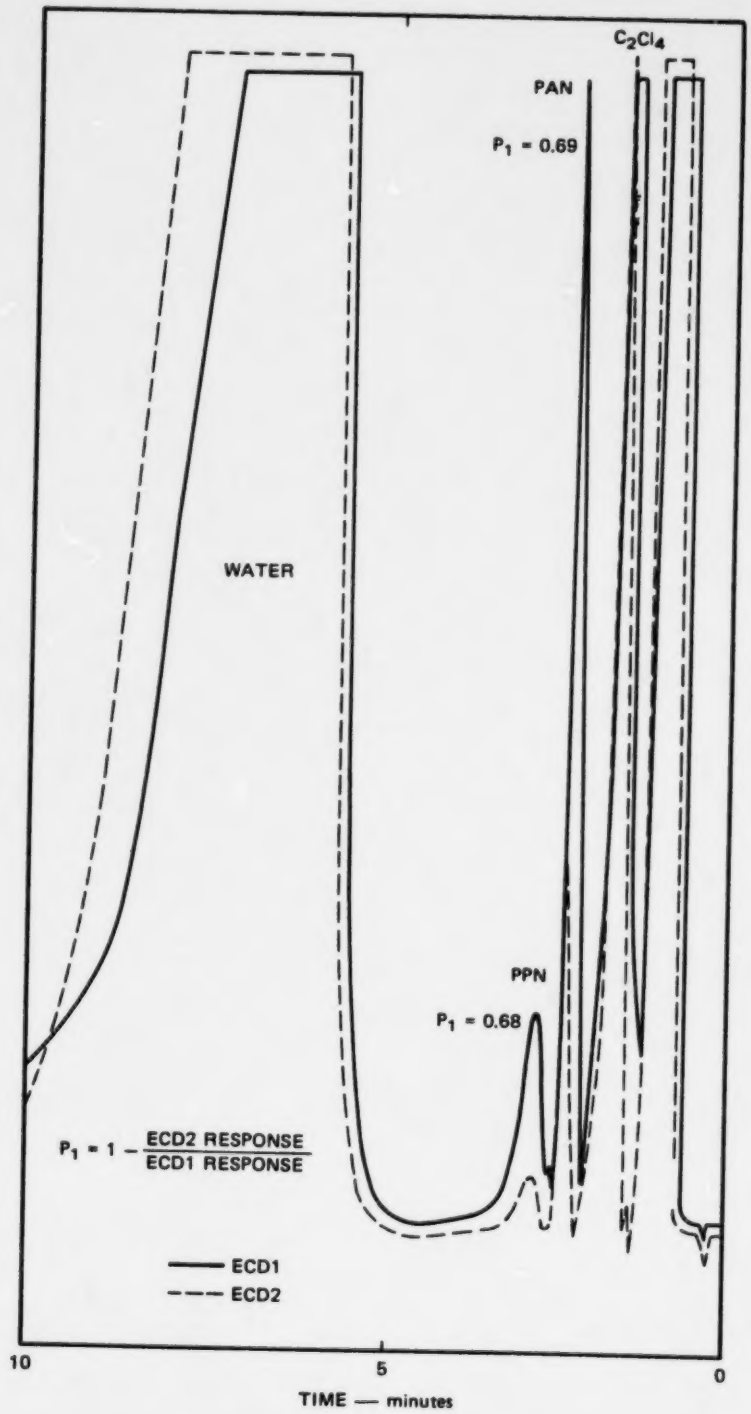


Figure 7. PAN and PPN separation from the air.

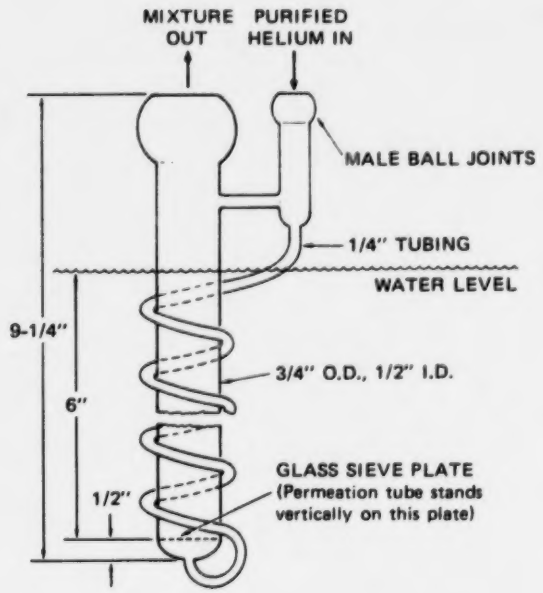


Figure 8. Permeation tube holder.

TABLE 7. PERMEATION RATE DATA FOR GENERATING PRIMARY STANDARDS.

Compound	Permeation Tube		Permeation Rate*			
	No.	Material†	µg/min	ppb/1/min (25°C, 1 atm)	Status	Quality
CH_2CHCHO	1910	FEP Teflon	1389	602	S	E
CH_2OCH_2	1908	FEP Teflon	1120	618	S	E
CCl_2F_2 (F-12)	6138	"Vial" type tube	615	123	S	E
CCl_3F (F-11)	1911	TFE Teflon	564	100	S	E
$CHCl_2F$ (F-21)	1941	FEP Teflon	26882	6340	S	E
CCl_2FCCl_2F (F-114)	1940	FEP Teflon	16253	2325	S	E
CCl_2FCC1F_2 (F-113)	1238	FEP Teflon	356	46	S	E
CH_3Cl	1905	FEP Teflon	2000	968	S	E
C_2H_5Cl	1232	FEP Teflon	354	134	S	E
CH_2CHCl	1900	FEP Teflon	3447	1348	S	E
CH_3Br	1893	FEP Teflon	1984	511	S	E
CH_3I	1239	FEP Teflon	181	31	S	G
CH_2Cl_2	1228	FEP Teflon	439	126	S	E
(cis) CHClCHCl	1939	FEP Teflon	2435	610	S	E
(trans) CHClCHCl	1898	TFE Teflon	1398	350	S	E
CCl_2CH_2	1897	TFE Teflon	731	183	S	E
CH_2ClCH_2Cl	1233	FEP Teflon	61	15	S	E
$COCl_2$	1909	FEP Teflon	3906	964	S	E
$CHCl_3$	1229	FEP Teflon	99	20	S	E
C_2HCl_3	1235	FEP Teflon	260	48	S	E
C_2Cl_4	1590	TFE Teflon	533	78	S	E
$CHBr_3$	1895	TFE Teflon	--‡	--	U(?)	P(?)
CH_3CCl_3	1896	TFE Teflon	--§	--	U	P
$CHClCHCl_2$	1906	TFE Teflon	--§	--	U	P
CH_2BrCH_2Br	1237	TFE Teflon	--§	--	U	P
CCl_4	1894	TFE Teflon	--§	--	U	P

*E–Excellent (errors in permeation rate $<\pm 5$ percent); G–Good (errors in permeation rate $<\pm 10$ percent); S–Satisfactory; U–Unsatisfactory; P–Poor.

†For many cases both FEP and TFE teflon tubing are satisfactory. C_2Cl_4 and CH_2ClCH_2Cl were exceptions with satisfactory performance only achieved for TFE and FEP materials respectively.

‡Nonlinear permeation rate.

§Permeation rate too slow to quantify.

those cases where permeation data is considered excellent (in Table 7) this is perhaps the best, most-accurate means of generating primary standards.

It is also clear from Table 7 that most of these perm tubes can be used to prepare standards directly at parts per billion (ppb) concentration levels. Batch dilutions were carried out to reduce these concentrations by a factor of 10^2 to 10^3. Over a wide range of concentration levels of several ppb's and low ppt's, the frequency-modulated ECDs that we used were completely linear. The linearity of the FID over a much larger concentration range is well known.

In addition to permeation tubes, standards were obtained from Scott-Marrin (Riverside, California). These were obtained at higher concentrations (5 to 10 ppm) for reasons of long-term stability. Table 8 lists the chemicals, the standard concentrations, and the cylinder materials. All of the chemicals were stored in aluminum cylinders except those containing CH_3Cl, which were contained in stainless-steel cylinders. Extreme care was required in selecting cylinder materials, since some of the chemicals (e.g., CH_3Cl) form unknown chemical complexes and could lead to potentially explosive conditions with aluminum.

All of the commercially obtained standards were rechecked with our permeation-tube standards when this was possible. The comparisons were found to yield excellent results (± 10 percent). The aromatic hydrocarbon standards were checked for carbon response against those available from NBS and found to agree within ± 5 percent. For other aromatic hydrocarbons carbon response derived from benzene and toluene responses was used.

For the chlorinated aromatics only Scott-Marrin standards were used: In the case of other chemicals for which no standards could be commercially obtained (e.g., $C_2H_2Cl_4$), batch standards were prepared at SRI. It was also assumed that isomers had identical ECD responses. In addition, the measured concentrations of some of the species (fluorocarbon-11 and CCl_4) were further checked by conducting absolute analysis with the aid of the gas-coulometric technique (Lillian and Singh, 1974; Singh et al., 1975). In the case of PAN and PPN, only gas-phase coulometry was used and the data must be considered preliminary until the confirmation of the reliability of PAN and PPN determination using gas-phase coulometry can be established. In the meantime, these data do appear reasonable. Calibration for total hydrocarbons, CO, and CH_4 were conducted in the field at least twice a day. NO_2 calibrations were conducted using a permeation tube as primary standard.

3. *Secondary Standards*

Except for the aromatic hydrocarbons, it was not possible to use primary standards during field operation. Therefore, an optimal scheme which depended on the use of secondary standards was devised.

Several 5-liter polished stainless-steel samplers were filled with urban air samples to a pressure of 35 to 40 psi. These were allowed to stabilize for one to two days and then analyzed by comparing them against the primary standards. The secondary standards were then used for field operation: Each GC channel was calibrated about 3 times a day with these secondary standards. The stability of nearly all species over a period of several days was found to be excellent. Figure 9 shows an example of the use of a single secondary standard during field operation. Some species such as PAN, PPN, or $COCl_2$ could not be stored for any reasonable length of time. This was not a serious hinderance since other chemicals could be used to ascertain the constancy of the ECD and the FID responses during field operations. All of the Scott-Marrin standards were also carried on board after these had been diluted to low ppb levels. These were also used as secondary standards (in addition to the collected air samples).

TABLE 8. PPM LEVEL PRIMARY STANDARDS IN AIR*

Standard and Compound	Concentration (ppm)	Cylinder	
		Type	Size (ft^3)
No. 1			
CH_3CCl_3	5.0		
CCl_4	5.2		
CH_2BrCH_2Br	5.0	Aluminum	30
C_2Cl_6	0.8		
No. 2			
C_6H_5Cl	5.0		
o-$C_6H_4Cl_2$	5.0	Aluminum	150
No. 3			
C_6H_6	5.0		
$C_6H_5CH_3$	5.0	Aluminum	150
No. 4			
CH_3Cl	10.0		
CH_2Cl_2	10.0	Stainless steel	30
CH_2ClCH_2Cl	10.0		
No. 5			
C_2HCl_3	10.0		
C_2Cl_4	10.0	Aluminum	30
$CHCl_3$	10.0		

*Obtained on order from Scott-Marrin, Inc., Riverside, California

D. *Quality Control*

Two major factors were critical in establishing the quality of the acquired data. These were the accuracy of primary standards and precision and repeatability of measurements. As stated earlier in this section, the primary standards commercially obtained were compared with our permeation tubes which can be routinely used to obtain reliable standards within errors of ± 5 to 10 percent. The aromatic hydrocarbon standards were compared with NBS propane standards and found to be accurate to within ±5 percent. The cross-calibrations between SRI generated standards with Scott-Marrin standards typically results in differences that were about ± 10 percent or less. The use of secondary standards nearly three times a day clearly demonstrated the excellent precision that was obtainable during field studies (Figure 9). The precision of reported field measurements is estimated to be ± 5 percent. The measurements presented here have an overall estimated accuracy of better than ± 15 percent.

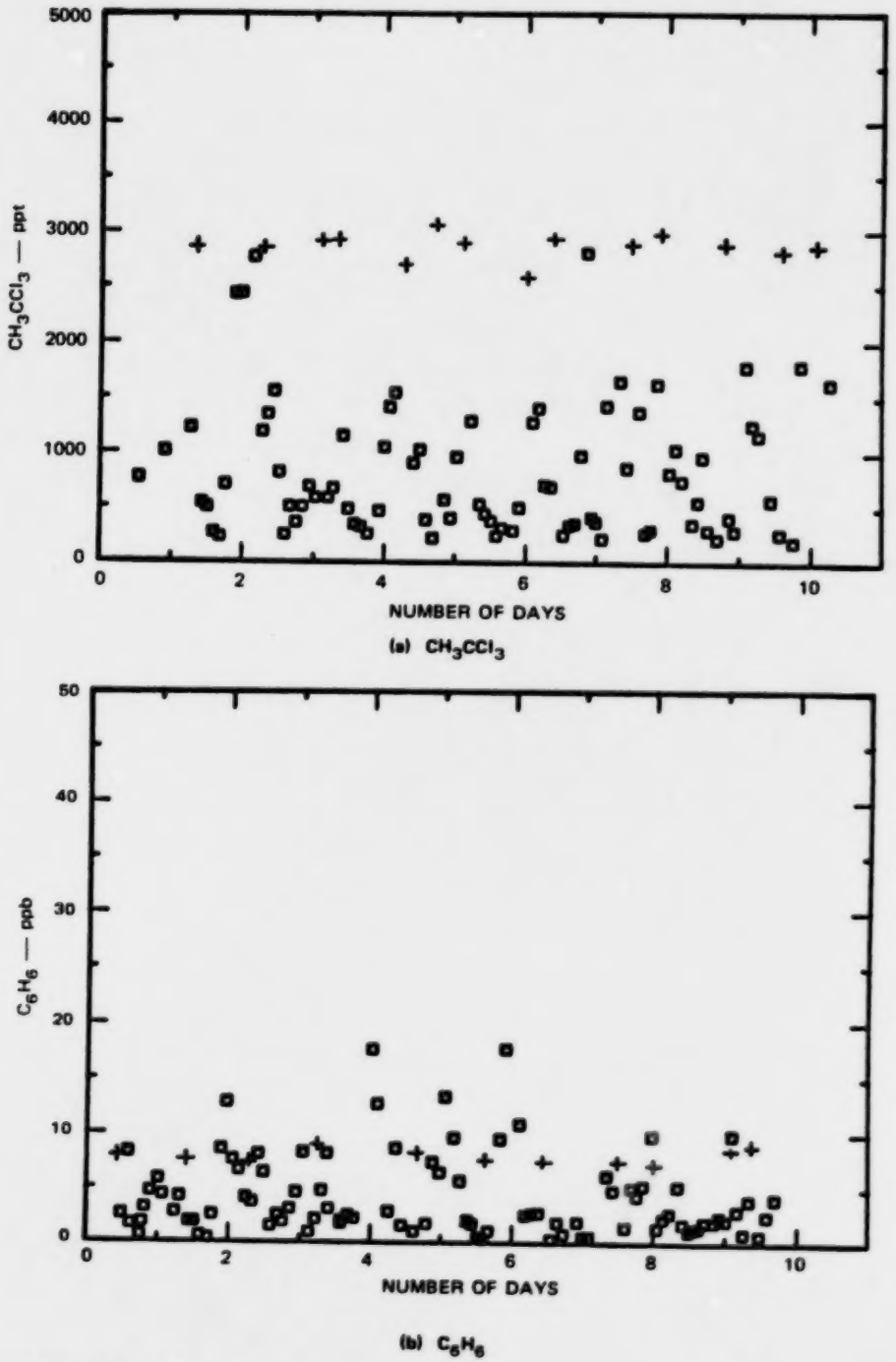


Figure 9. Secondary standard response for 1,1,1 trichloroethane and benzene in Phoenix — Site 2.

SECTION 5

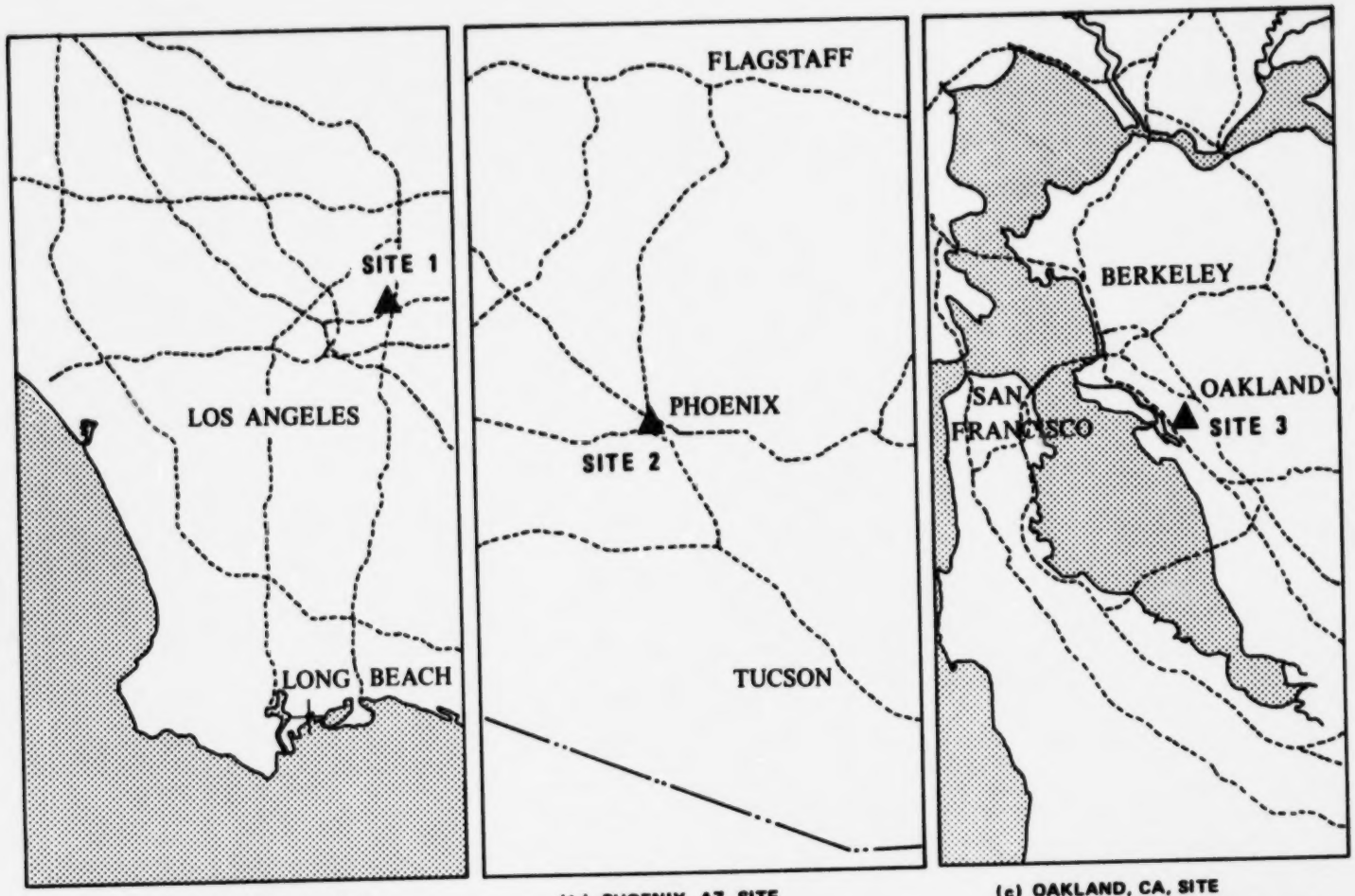
FIRST YEAR PLAN OF FIELD MEASUREMENTS

The first quarter of this project was devoted to developing methods for accurately analyzing a comprehensive list of toxic chemicals and to procuring supplies and equipment for the three planned field studies.

After the measurement methodology was developed, field studies were conducted in selected urban sites. The three sites selected were in Los Angeles, California; Phoenix, Arizona; and Oakland, California. In all cases, the sites were near the downtown areas but represented an open urban atmosphere. There were no nearby sources or topographical features that could directly affect the representativeness of the measurements. The Los Angeles and Phoenix field programs were conducted in late May and early June 1979; the Oakland measurements were completed in early July. Figure 10 shows the location of these sites and the period of field operation. Each field study was of about two weeks duration. Despite the logistical difficulty, a 24-hour measurement schedule offers the most efficient means of collecting the maximum amount of data to characterize the burden of toxic organic chemicals in the ambient air. In addition, night abundances of trace chemicals are likely to provide crucial information about the sources and sinks of measured species. Therefore, during all field programs a 24 hour per day measurement schedule was followed.

Ambient measurements of toxic chemicals were complemented by conducting limited exploratory measurements from indoor atmospheres. These indoor air samples were collected in specially treated stainless-steel sampling vessels of 1 to 5 liters in volume and were pressurized to 35 psi.

Although meteorological analysis has not yet been completed, general weather conditions were not unusually stagnant. At Site 1, meteorological conditions lead to good convective activity resulting in relatively low pollutant levels. Site 2 was most characteristic in its meteorological behavior: High afternoon temperatures (>90°F) and low relative humidity caused deep vertical mixing to occur in the afternoon. Cold nights, however, created a shallow nocturnal inversion. Site 3 seemed to be impacted by transport from upwind commercial and industrial sources: San Francisco and downtown Oakland were also upwind of this site. This is consistent with typical trajectories in this region. No significant night accumulation is seen at Site 3 (probably because of reverse drainage).



(a) LOS ANGELES, CA, SITE (34°04'N, 118°09'W; measurement period 4/9/79 – 4/21/79)

(b) PHOENIX, AZ, SITE (33°28'N, 112°06'W; measurement period 4/23/79 – 5/06/79)

(c) OAKLAND, CA, SITE (37°45'N, 122°11'W; measurement period 6/28/79 – 7/10/79)

Figure 10. Location of sites selected for field studies.

SECTION 6

ESTIMATED RESIDENCE TIME OF MEASURED CHEMICALS IN POLLUTED ATMOSPHERES

It is well known that hydroxyl radical (HO) plays a central role in depleting atmospheric organics, both in the polluted and the clean atmospheres. A knowledge of the atmospheric loss rate of a chemical is essential for the interpretation of field data and for the eventual prediction of the fate of a toxic chemical. For species of Table 9 we have concluded that no significant error is incurred when reactions with species other than HO, namely $O(^3P)$, O_3, HO_2, etc. are neglected. Table 9 lists the chemical residence time of the organic species measured in this study based on a daily average (24 h) HO abundance of 10^6 molec/cc. This is equivalent to a daytime (12 h) HO abundance of 2×10^6 molec/cc. These HO levels are well supported by available field data (Calvert, 1976; Singh et al., 1979a). It is noted that a daily average (24 h) HO concentration of 10^6 molec/cc is probably typical of urban environments in summer months. In wintertime these HO levels are expected to be lower by a factor of about 2. The residence times $\tau_c(sec) = 1/[k(HO]$ would be correspondingly longer. The residence time of PAN and PPN are largely determined by thermal decomposition and are estimated from Hendry and Kenley (1979). Because of its strong temperature dependence, the residence times of PAN and PPN can be two orders of magnitude longer in colder winter locations. The rate constant data are taken from JPL (1979) and estimated from Hendry (1979). The percentage loss in one day $[1 - \exp(-1/\tau_c)]$ is also estimated in Table 9. It is clear from Table 9 that toxic chemicals with residence times that vary from less than an hour to several years exist in polluted atmospheres.

TABLE 9. ESTIMATED RESIDENCE TIMES AND DAILY CHEMICAL LOSS RATES OF SELECTED TOXIC CHEMICALS

Chemical Name	Chemical Formula	Rate Constant $10^{12} \times k_{HO}$* (300°K)	Residence Times τ_c† (days)	Percent Loss in One Day (or 12 sunlit h)
Methyl chloride	CH_3Cl	0.05	231	0.4
Methyl bromide	CH_3Br	0.04	289	0.4
Methylene chloride	CH_2Cl_2	0.15	77	1.3
Chloroform	$CHCl_3$	0.10	116	0.9
Carbon tetrachloride	CCl_4	<0.001	>11600	≈0.0
1,1 Dichloroethane	CH_3CHCl_2	0.26	44	2.3
1,2 Dichloroethane	CH_2ClCH_2Cl	0.22	53	1.9
1,2 Dibromoethane	CH_2BrCH_2Br	0.25	46	2.2
1,1,1 Trichloroethane	CH_3CCl_3	0.02	579	0.2
1,1,2 Trichloroethane	$CH_2ClCHCl_2$	0.02	579	0.2
1,1,1,2 Tetrachloroethane	CH_2ClCCl_3	<0.01	>1160	<0.1
1,1,2,2 Tetrachloroethane	$CHCl_2CHCl_2$	<0.01	>1160	<0.1
Hexachloroethane**	CCl_3CCl_3	<0.001	>11600	≈0.0
Vinyl chloride	CH_2CHCl	6.6	1.8	42.6
Vinyledene chloride	CH_2CCl_2	4.0‡	2.9	29.2
1,2 Dichloroethylene	$CHClCHCl$	4.0	2.9	29.2
Trichloroethylene	$CHClCCl_2$	2.2	5.3	17.2
Tetrachloroethylene	CCl_2CCl_2	0.17	68	1.5
Chlorobenzene	C_6H_5Cl	0.4‡	29	3.4
m-Dichlorobenzene	m-$C_6H_4Cl_2$	0.07‡	165	0.6
p-Dichlorobenzene	p-$C_6H_4Cl_2$	0.07‡	165	0.6
o-Dichlorobenzene	o-$C_6H_4Cl_2$	0.07‡	165	0.6
Trichlorobenzene	$C_6H_3Cl_3$	0.01‡	1160	<0.1
Benzene	C_6H_6	1.4	8.3	11.4
Toluene	$C_6H_5CH_3$	6.0	1.9	40.9
Ethylbenzene	$C_6H_5C_2H_5$	8.0	1.4	51.0
m-Xylene	m-$C_6H_4(CH_3)_2$	23.4	0.5	86.5
p-Xylene	p-$C_6H_4(CH_3)_2$	12.3	0.9	67.0
o-Xylene	o-$C_6H_4(CH_3)_2$	13.9	0.8	71.3
4-Ethyl toluene	4-$C_6H_4C_2H_5CH_3$	12.9	0.9	67.0
1,2,4 Trimethylbenzene	1,2,4 $C_6H_3(CH_3)_2$	33.2	0.3	96.4
1,3,5 Trimethylbenzene	1,3,5 $C_6H_3(CH_3)_2$	49.3	0.2	99.3
Phosgene	$COCl_2$	—	—	—
Peroxyacetyl nitrate	$CH_3COOONO_2$	—	0.05§	99.9
Peroxypropionyl nitrate	$CH_3CH_2COOONO_2$	—	<0.05§	99.9

*Rate constant with hydroxyl radical (HO) in units of cm^3 $molec^{-1}$ sec^{-1}

†Calculated based on an estimated average daily (24 h) HO abundance of 10^6 molec/cc; corresponds to a daytime average (≈12 h) HO concentration of 2×10^6 molec/cc.

‡Estimated from Hendry (1979)

§Thermal degradation in the presence of NO and NO_2

**Not measured

SECTION 7

ANALYSIS OF FIELD DATA

Experiments at all sites were satisfactory and no breakdowns of a serious nature were encountered. Because of our decision to operate on a 24-hour basis, a vast amount of data was collected. The entire catalog of data on toxic organic chemicals has been processed and a master data file has been created. The meteorological and inorganic chemical (such as O_3, NO, NO_2) data have not been processed. All of the meteorological information, however, is also accessible directly from chart paper. The toxic-chemical master data file will be updated as additional field studies are conducted. Currently this master file is easily accessible for data processing.

A. *Atmospheric Abundances, Daily Doses, Fates and Variabilities of Measured Species*

Table 10 summarizes data on all of the toxic chemicals measured during the three field studies; maximum, minimum, and average concentration are presented for each of the measured species. The quantity in parenthesis is the standard deviation associated with the average concentration. The averages and standard deviations are calculated from actual data acquired and involve no interpolations. In addition, Table 10 presents an average daily outdoor dose for each of the species and the standard deviation associated with this average daily dose. This dose is determined (based) on an average air intake of 23 m^3 at 25°C and 1 atm for a 70 kg male (NAS, 1978). The daily doses were calculated by linear interpolation between measured field data. The reported dose in Table 10 represents the average of daily average doses and the standard deviations associated with this overall average dose.

Much of the information in Table 10 is self-explanatory, so only salient observations will be made here. Table 11 summarizes the total average exposure to each chemical category (defined in Table 10) for the three sites; note that not all of the chemicals in a given category (e.g., CH_3Cl and CH_3Br) are equally toxic. The following sections discuss each of the individual species by given category.

B. *Data Analyses by Chemical Category*

1. *Halomethanes*

Table 10 shows that methyl chloride, methyl bromide, methylene chloride, chloroform, and carbon tetrachloride are the five species of most interest in this category. Table 12 provides a brief summary of sources, release rates, and uses of these five species: The following sections discuss the abundance, fate, and diurnal variability of each. The average dose for the entire halomethane grop was 516, 253, and 124 μg/day at Sites 1, 2, and 3 respectively (Table 11).

TABLE 10. CONCENTRATIONS AND DAILY OUTDOOR DOSAGE OF MEASURED CHEMICAL SPECIES AT SELECTED SITES

Chemical Group and Species	Los Angeles – Site 1 (4/9/79–4/21/79)						Phoenix – Site 2 (4/23/79–5/06/79)						Oakland – Site 3 (6/28/79–7/10/79)					
	Concentration*				Dose† (μg/day)		Concentration				Dose (μg/day)		Concentration				Dose (μg/day)	
	Mean	S.D.‡	Max.	Min.	Average	S.D.	Mean	S.D.	Max.	Min.	Average	S.D.	Mean	S.D.	Max.	Min.	Average	S.D.
Halomethanes																		
Methyl chloride	3001.6	1759.0	7761.0	1037.9	140.4	56.8	2390.9	940.0	5685.3	1230.7	108.6	19.6	1066.2	780.9	4999.8	483.7	59.7	47.6
Methyl bromide	244.1	193.7	894.2	13.0	24.5	12.6	66.8	47.2	189.6	3.7	6.2	1.9	54.7	24.0	108.3	25.8	4.5	0.7
Methylene chloride	3751.1	2620.3	12028.8	601.4	308.9		893.6	988.6	5155.2	85.9	86.3	41.7	415.5	314.6	2405.8	85.9	33.0	9.1
Chloroform	88.2	39.9	223.5	24.3	10.5	3.3	111.4	106.0	514.0	27.1	12.1	4.2	32.1	12.1	60.1	13.1	3.7	0.8
Carbon tetrachloride	215.1	107.0	994.8	96.8	32.1	7.3	276.5	114.2	855.3	130.5	39.5	4.7	168.5	132.5	986.6	94.3	23.1	4.0
Fluorocarbons																		
Trichloro-monofluoro-methane	472.6	196.9	1069.7	220.7	59.3	14.9	249.3	138.1	721.9	110.0	34.7	9.8	238.9	150.7	1477.4	107.9	31.1	7.4
Trichloro-trifluoro-ethane	304.8	667.1	4160.1	48.8	48.3	59.9	151.3	224.7	1251.3	12.2	42.2	31.6	49.4	59.1	308.8	16.3	9.2	3.5
Haloethanes																		
1,2 Dichloroethane	518.6	232.9	1353.0	173.0	78.6	17.4	215.9	219.5	1449.6	38.7	27.2	33.1	82.8	106.1	841.9	38.3	7.9	3.8
1,2 Dibromoethane	33.2	26.2	187.2	5.4	6.0	2.7	40.3	38.3	204.4	2.4	7.0	2.7	15.8	12.5	84.5	2.4	2.9	0.8
1,1,1 Trichloroethane	1028.1	646.3	5143.7	224.2	133.0	44.6	823.5	597.4	2813.6	197.8	116.0	38.6	290.9	160.6	967.2	142.9	38.3	11.0
1,1,2 Trichloroethane	9.3	5.9	45.3	3.6	1.1	0.4	16.1	10.2	42.3	0(<1) f=0.39	0.9	0.6	7.9	4.4	28.5	3.6	0.9	0.3
1,1,1,2 Tetrachloroethane	3.7	2.3	12.4	0(<1)	0.4	0.3	8.5	3.9	16.2	0(<1) f=0.08	0.1	0.3	4.2	1.3	8.0	0(<1) f=0.97	0.6	0.1
1,1,2,2, Tetrachloroethane	16.6	11.3	95.8	4.4	2.7	0.9	17.0	6.4	31.3	0(<1) f=0.78	2.1	0.8	7.1	2.6	13.4	3.1	1.1	0.2
Choroethylenes																		
Vinyledene chloride	4.9	2.8	9.7	1.0	0.4	0.1	29.8	36.8	15.8	0(<1) f=0.90	2.5	1.5	12.6	5.1	24.4	4.8	1.1	0.2
1,2 (cis) dichloroethylene	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Trichloroethylene	399.1	302.1	1702.2	36.3	58.3	32.7	483.5	586.9	3069.6	11.7	75.6	58.0	187.6	269.7	1558.2	14.1	19.7	8.7
Tetrachloroethylene	1479.7	444.5	2065.3	173.5	235.5	31.4	993.8	715.5	3696.8	129.1	172.7	32.4	308.4	291.6	1449.8	53.4	45.9	21.9

Table 10. (continued)

Chemical Group and Species	Los Angeles – Site 1 (4/9/79–4/21/79)						Phoenix – Site 2 (4/23/79–5/06/79)						Oakland – Site 3 (6/28/79–7/10/79)					
	Concentration*				Dose† (µg/day)		Concentration				Dose (µg/day)		Concentration				Dose (µg/day)	
	Mean	S.D.‡	Max.	Min.	Average	S.D.	Mean	S.D.	Max.	Min.	Average	S.D.	Mean	S.D.	Max.	Min.	Average	S.D.
Chlorobenzenes																		
Monochlorobenzene	≈200	---	≈500	<50	≈21	---	≈200	---	≈500	<50	≈21	---	≈100	---	≈300	<50	10	---
o-Dichlorobenzene	125.4	98.8	503.9	23.3	18.8	10.0	226.0	348.1	2357.6	11.4	27.7	17.4	39.9	50.3	326.1	10.3	4.9	1.5
m-Dichlorobenzene	77.3	56.1	253.6	15.4	11.4	3.6	87.0	58.5	277.1	5.1	10.8	2.6	65.3	29.0	146.4	25.6	8.4	2.3
1,2,4 Trichlorobenzene	69.3	48.8	339.4	19.7	11.8	5.5	30.8	21.2	101.5	8.7	4.8	1.4	29.5	23.7	151.2	9.7	6.3	4.7
Aromatic hydrocarbons																		
Benzene (ppb)	6.04	4.58	27.87	0.72	424.1	202.2	4.74	6.75	59.89	0.39	349.7	155.5	1.55	1.22	4.63	0.06	105.12	40.9
Toluene (ppb)	11.72	9.07	53.38	1.14	1027.7	421.4	8.63	9.09	38.73	0.54	705.2	288.1	3.11	3.18	16.94	0.15	260.58	86.9
Ethyl benzene (ppb)	2.25	4.47	27.66	0.10	213.0	169.0	2.00	2.87	16.64	0.06	182.0	78.0	0.60	0.67	4.58	0.06	59.0	29.0
m/p-Xylene (ppb)	4.61	6.14	49.96	0.53	439.0	217.0	4.20	4.66	26.97	0.21	419.0	161.0	1.51	1.42	8.26	0.10	151.0	51.0
o-Xylene (ppb)	1.93	1.83	12.74	0.09	192.0	84.0	1.78	1.88	9.19	0.04	171.0	61.0	0.77	0.73	4.05	0.08	69.0	22.0
4-Ethyl toluene (ppb)	1.51	1.45	10.15	0.10	175.1	79.1	1.51	1.50	7.37	0.20	169.5	58.7	0.66	0.62	3.40	0.02	65.5	13.6
1,2,4 Trimethyl benzene (ppb)	1.88	2.38	13.29	0.17 f=0.78	195.5	111.9	1.74	1.91	10.09	0.02 f=0.68	201.1	72.3	---	---	---	---	---	---
1,3,5 Trimethyl benzene (ppb)	0.38	0.68	5.02	0(<0.04)	33.9	22.6	0.40	0.37	1.52	0(<0.04)	30.5	12.4	---	---	---	---	---	---
Secondary organics																		
Phosgene	---	---	---	---	---	---	---	---	---	---	---	---	49.7	5.1	56.7	42.2	4.6	0.5
Peroxyacetyl nitrate (PAN)	4977.3	4482.7	16820.0	30.0	550.3	276.5	778.9	767.1	3720.0	0(<0.02)	85.9 f=0.99	27.2	355.9	421.5	1850.0	50.0	32.3	13.1
Peroxypropionyl nitrate (PPN)	721.5	672.8	2740.0	0(<0.03)	77.0 f=0.86	50.3	93.1	77.1	330.0	0(<0.03)	5.5 f=0.47	2.0	149.2	117.9	500.0	0(<0.03)	16.4 f=0.25	6.0

*Concentrations for all groups in ppt except aromatic hydrocarbon concentrations in ppb; frequency of occurrence (f) of a detectable concentration always = 1 unless otherwise given.

†Based on total air intake of 23 m^3/day at 25°C; 1 atm pressure.

‡Standard Deviation.

TABLE 11. AVERAGE DAILY EXPOSURE TO MEASURED CHEMICAL GROUPS

Chemical Category*	Total Average Daily Dose (μg/day)		
	Los Angeles (Site 1)	Phoenix (Site 2)	Oakland (Site 3)
Halomethanes	516	253	124
Haloethanes	222	153	52
Chloroethylenes	292	251	67
Chloroaromatics	63	65	30
Aromatic hydrocarbons	2700	2228	710
Secondary organics	627	91	54
Total	4420	3041	1037

*Fluorinated species such as fluorocarbons are excluded. For the constituents in each category see Table 10.

TABLE 12. PRODUCTION, EMISSIONS, AND USAGES OF IMPORTANT HALOMETHANES

Compound	Source*	U.S. Production (million metric tons)	Emissions (%)	Usage and Remarks
CH_3Cl	A,N(O)	0.25 (1973)	5–10	85% of production used for manufacture of silicones and tetramethyl lead intermediates; large natural source (≈3 million tons/yr) identified in the ocean
CH_3Br	A,N(O)	0.02 (1977)	≈50	Soil fumigant
CH_2Cl_2	A	0.32 (1977)	80–90	55% of production used for paint removing and solvent degreasing
$CHCl_3$	A	0.14 (1976)	5–10	Manufacture of fluorocarbon-22
CCl_4	A	0.53 (1974)	5–10	Manufacture of fluorocarbons-11 and -12

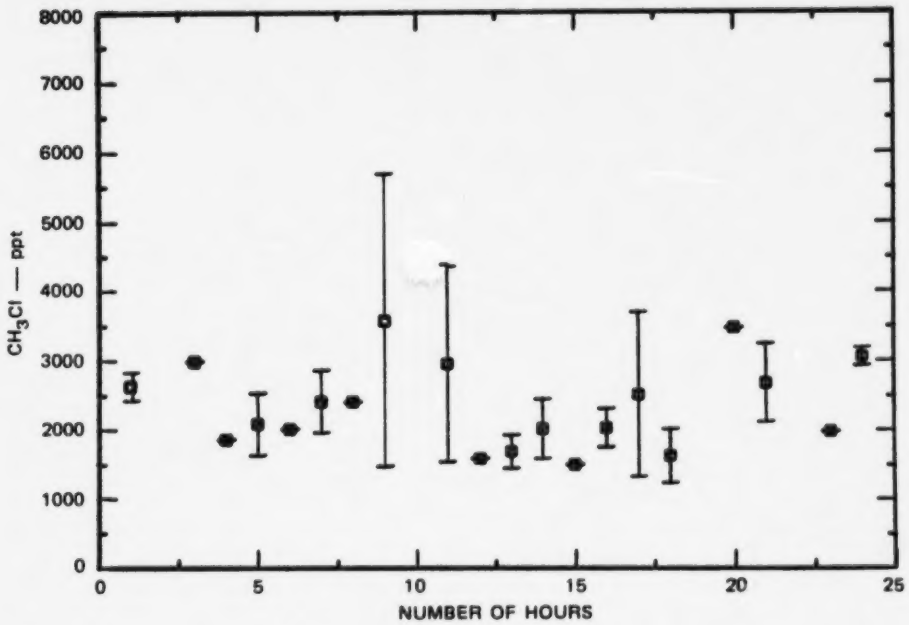
*A – anthropogenic; N – natural; O – oceanic source.
Source: A.D. Little (1975); Singh et al. (1979)

Methyl Chloride (CH_3Cl)—Methyl chloride was found to be far more abundant in the urban atmosphere when compared with its background concentration of 0.6 ppb (Singh et al., 1979). Concentration levels as high as 7.8, 5.7, and 5.0 ppb were measured at the three sites as shown in Table 10. The highest measured concentrations were a factor of 5 to 10 larger than the lowest measured concentration. The lowest levels were 1 to 2 times the background levels. The average concentration of 3.0, 2.4, and 1.1 ppb at Sites 1, 2, and 3 respectively further point to significantly elevated CH_3Cl levels in urban environments. Average daily doses of 140, 109, and 60 μg/day are calculated for Sites 1, 2, and 3 respectively. These should be compared with a daily dose of 40 μg/day for unpolluted environments. Elevated CH_3Cl levels in urban environments may be related possibly to combustion sources but are currently unexplained. Methyl chloride is slowly depleted in the atmosphere, and chemical loss of less than 0.5 percent per day is estimated (Table 9). Figure 11 demonstrates the lack of a significant diurnal variability in the atmospheric abundance of CH_3Cl: A slight afternoon minimum at Site 2 can be observed. Methyl chloride is generally not considered to be highly toxic (NAS, 1978).

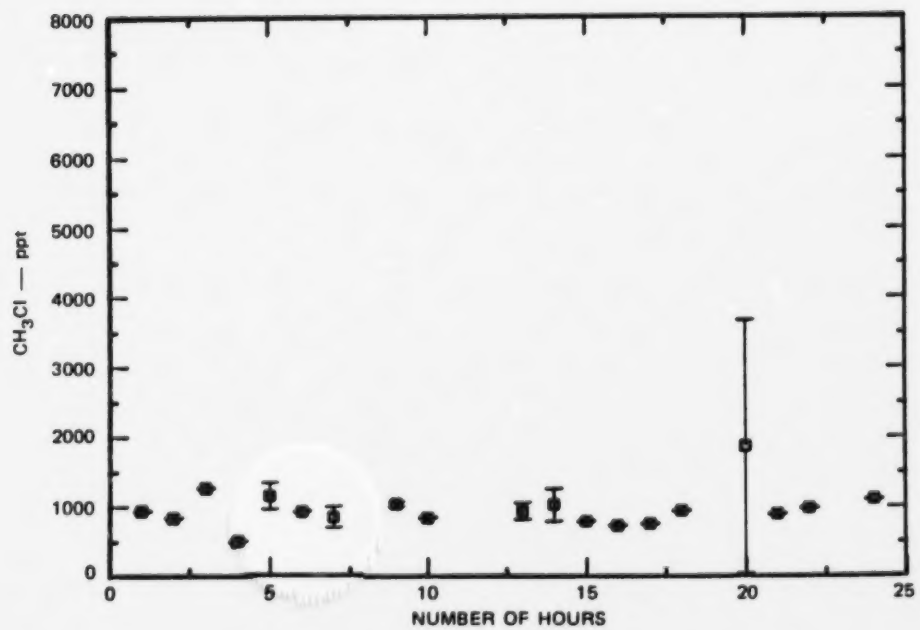
Methyl Bromide (CH_3Br)—Methyl bromide is considered to be significantly more toxic than methyl chloride (NAS, 1978). Its levels were significantly elevated above the background (5 to 20 ppt) at all three sites. Average concentrations of 0.24, 0.07, and 0.05 ppb were measured at Sites 1, 2, and 3 respectively. The highest concentration level of 0.9 ppb was measured in Los Angeles (Site 1). The lowest measured concentrations of CH_3Br were comparable to the expected background (Singh et al., 1979). A daily average dose of 25, 6, and 5 μg/day was calculated for the three sites respectively. The sources of CH_3Br in the urban environment constitute direct losses when CH_3Br is used as a fumigant. However, automotive sources of CH_3Br, possibly resulting from the catalytic decomposition of CH_2BrCH_2Br have also been suggested (NAS, 1978). No significant diurnal variations were observed. Average diurnal variation at Sites 2 and 3 (Figure 12) indicated a slight depression in the afternoon concentrations at the Phoenix site and a slight elevation at the Oakland site. The diurnal variation at the Los Angeles site showed greater scatter but indicates somewhat-reduced afternoon levels. The diurnal variation, if any, must be controlled by emission sources (local and from transport) and meteorological processes, since CH_3Br is too unreactive to undergo significant chemical loss (< 0.5 percent per day) on a daily basis (Table 9). As stated earlier, the pronounced afternoon minimum at Site 2 is attributable to deep vertical mixing (high temperatures and low relative humidity), while the afternoon maximum at Site 3 represents transport from sources upwind.

Methylene Chloride (CH_2Cl_2)—Methylene chloride is a large volume solvent that has been increasingly popular in recent years. The toxicity of CH_2Cl_2 is a matter of considerable debate but high exposure is clearly evident. Average concentrations of 3.8, 0.9, and 0.4 ppb (Table 10) were measured at Sites 1, 2, and 3 respectively. The highest concentration, 12 ppb, was measured in Los Angeles (Site 1): Even the lowest measured levels at Site 1 were an order of magnitude higher than the Northern Hemisphere background concentration of CH_2Cl_2 ($\sim$ 45 ppt). The lowest levels measured at Sites 2 and 3 were about twice the background concentration. A daily average dose of 310, 86, and 33 μg/day is estimated for Sites 1, 2, and 3 respectively. In remote environments, this exposure will be somewhat less than 4 μg/day.

The diurnal variation of CH_2Cl_2 typically consisted of somewhat elevated levels in the late-evening and early-morning hours. Figure 13 shows the diurnal variation of CH_2Cl_2 at Sites 1 and 2. The amplitude of the diurnal variation was significant only at Site 2. As discussed earlier, high afternoon temperatures and low relative humidity at Site 2 result in deep vertical mixing, causing an afternoon minimum. This minimum in CH_2Cl_2 concentration can not be attributed to chemical loss mechanisms. We estimate that daily CH_2Cl_2 chemical depletion rate over a polluted region is less than 2 percent per day (Table 9).

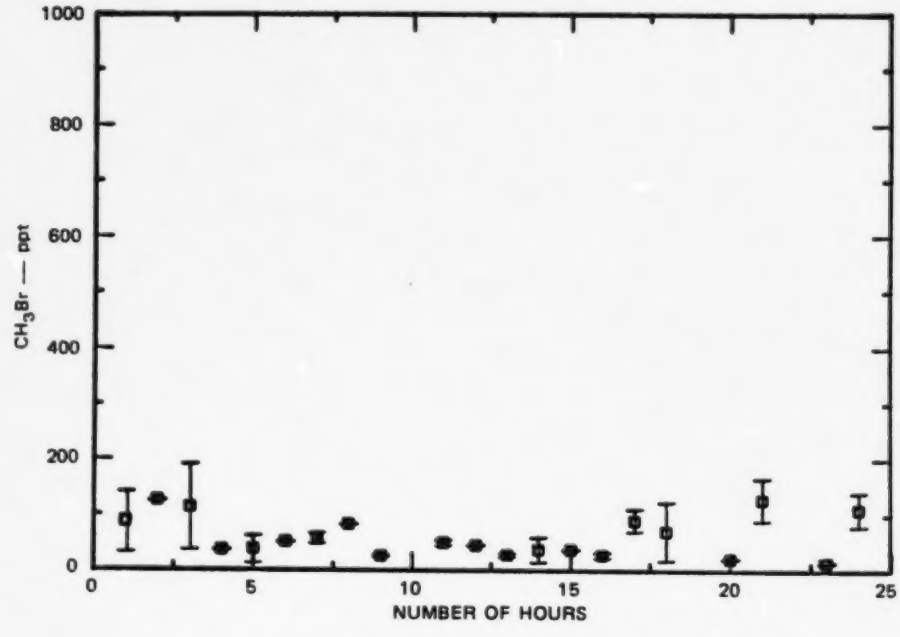


(a) SITE 2 — PHOENIX

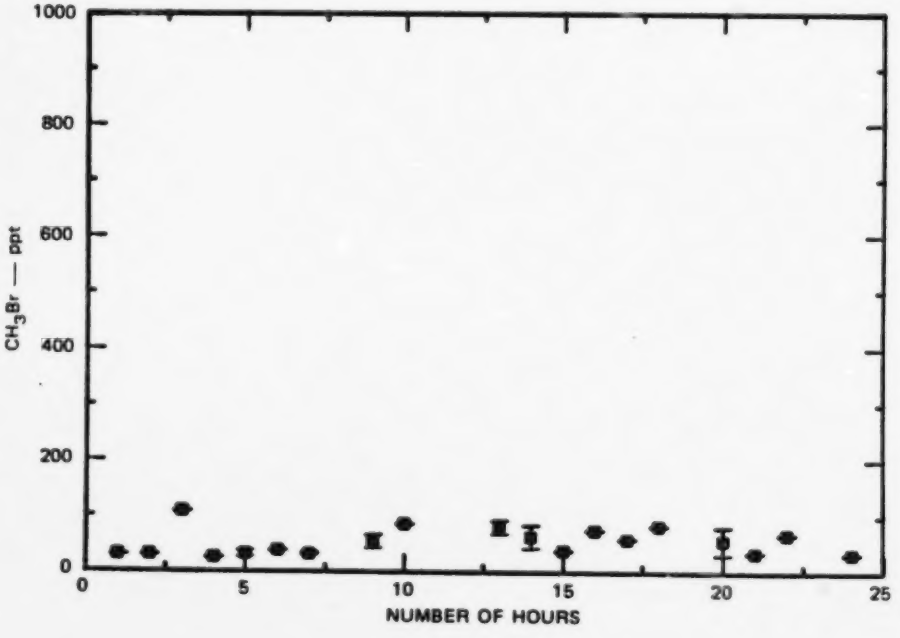


(b) SITE 3 — OAKLAND

Figure 11. Average diurnal variation of methyl chloride.

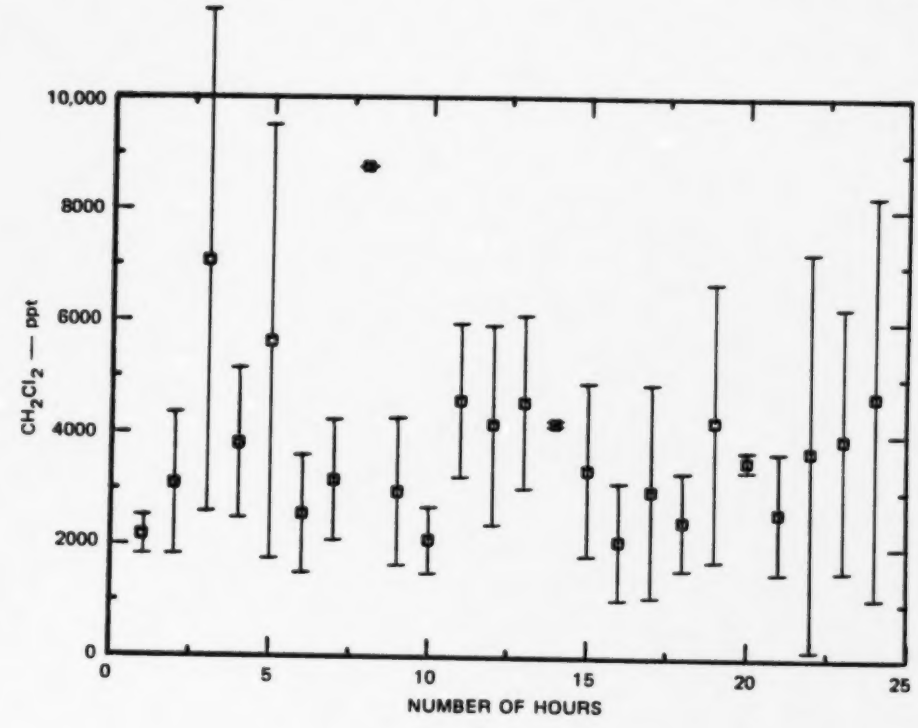


(a) SITE 2 — PHOENIX

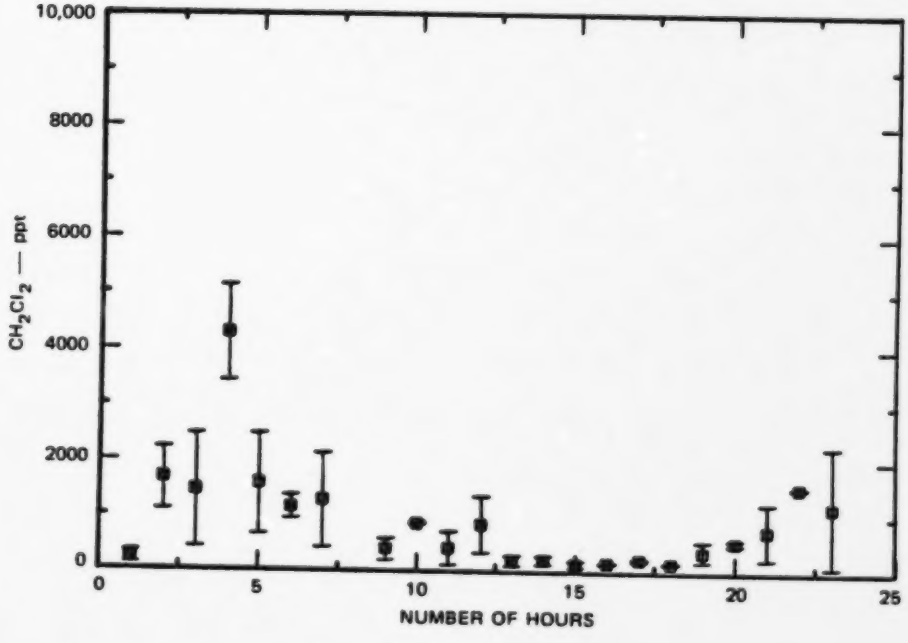


(b) SITE 3 — OAKLAND

Figure 12. Average diurnal variation of methyl bromide.



(a) SITE 1 — LOS ANGELES



(b) SITE 2 — PHOENIX

Figure 13. Average diurnal variation of methylene chloride.

Chloroform ($CHCl_3$)—We have previously determined the background concentration of $CHCl_3$ in the Northern Hemisphere to be about 15 ppt (Singh et al., 1979). It is clear from Table 9 that the urban levels of $CHCl_3$ areas significantly elevated. The highest $CHCl_3$ concentration of 0.5 ppb was measured at Site 2: Average concentrations of 0.09, 0.11, and 0.03 ppb were measured at Sites 1, 2, and 3 respectively. The lowest measured concentrations were within 1 to 2 times the expected levels. Chloroform is a suspected carcinogen (CEN, 1976) and may pose a significant hazard even at low exposure levels: Average daily doses of 11, 12, and 4 μg/day are determined for Sites 1, 2, and 3 respectively. The urban sources of $CHCl_3$ are poorly characterized but include both direct primary emissions as well as secondary emissions from water sources that have undergone chlorination. In both Los Angeles and Oakland a mild diurnal variation with somewhat higher levels in the early morning and late evening was observed. Once again a dramatic afternoon minimum was evident at the Phoenix site, as shown clearly in Figure 14. As explained earlier the causes of this minimum are exclusively meteorological, since $CHCl_3$ chemical depletion rate is expected to be only about 1 percent per day (Table 9).

Carbon Tetrachloride—CCl_4 is suspected to be a carcinogen and is nearly uniformly distributed in the global atmosphere. This is largely a result of the virtual absence of removal mechanisms, such that CCl_4 has an atmospheric residence time that can be measured in decades (Table 9). CCl_4 is not, however, a constituent of the natural atmosphere (Singh et al., 1976). The average background concentration of CCl_4 has been measured at about 110-130 ppt (Singh et al., 1979). The lowest levels of CCl_4 measured at Sites 1, 2, and 3 are comparable to the expected background concentration. The average levels of 0.22, 0.28, and 0.17 ppb at Sites 1, 2, and 3, respectively, clearly demonstrate the somewhat elevated urban levels. (These averages, however, are within a factor of 1 to 2 of the background CCl_4 levels.) At all three sites maximum concentration levels approaching 1 ppb were measured. The average CCl_4 daily dose of 32, 40, and 23 μg/day can be calculated for Sites 1, 2, and 3, respectively compared with an average daily dose of about 17 μg/day even in the clearest environment.

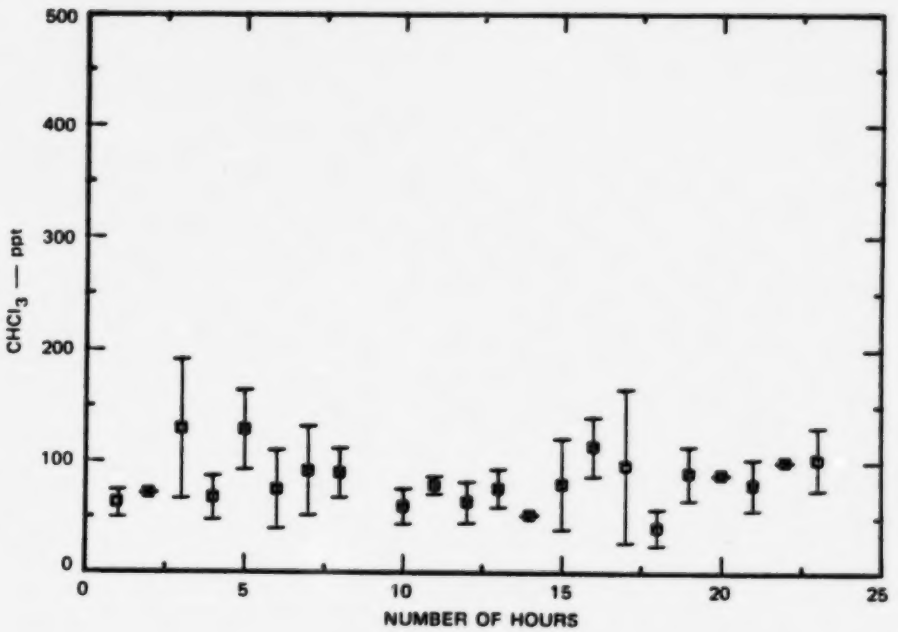
CCl_4 showed little variation at all three sites. Its variability is better demonstrated from a look at the raw data shown in Figure 15. There is evidence of source activity in the early-morning hours at Site 1 and 2. Levels at Site 3 changed little but occasional spikes were observed.

2. *Haloethanes*

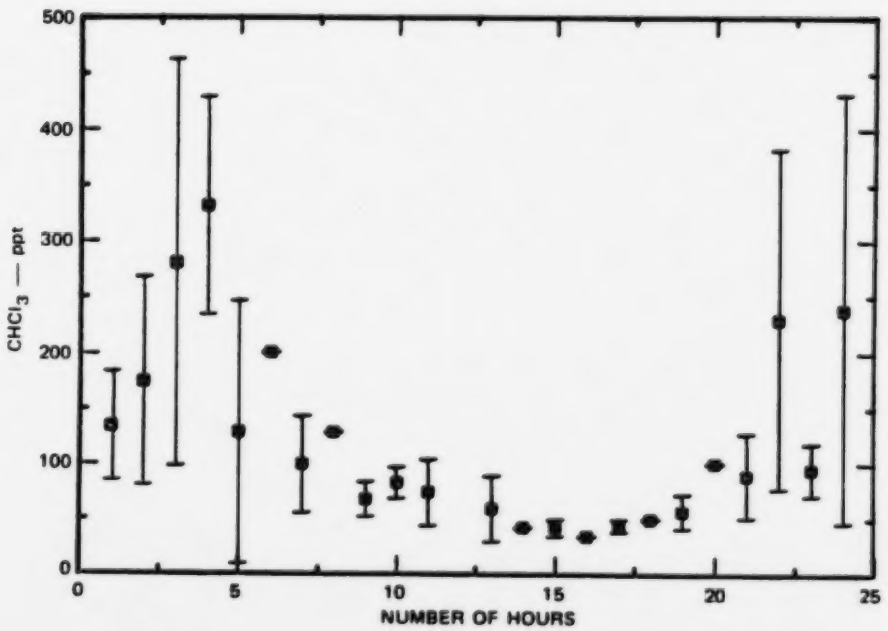
Unlike some halomethanes (e.g., CH_3Cl and CH_3Br), haloethanes are completely man-made and do not constitute a part of the unperturbed natural atmosphere. A wide variety of haloethanes are used in industrial and commercial activities. Table 13 provides a summary of the sources, production, release, and usages of some of the selected haloethanes. The six haloethanes measured are discussed below.

1,2 Dichloroethane (CH_2ClCH_2Cl)—This large-volume chemical is manufactured for use as a starting material in the synthesis of vinylchloride, vinyledene chloride, and chloroethylenes (CIS, 1979). Since 1,2 dichloroethane is a suspected carcinogen (Albert, 1978), exposure to this chemical is of considerable interest. Table 10 indicates maximum concentration levels of 1.4, 1.4, and 0.8 ppb measured at Sites 1, 2, and 3, respectively. Average concentrations at these sites respectively were 0.52 ppb at Site 1, 0.22 ppb at Site 2, and 0.08 ppb at Site 3.

The daily average dose is calculated to be 79, 27, and 8 μg/day respectively for Sites 1, 2, and 3. The diurnal variation of CH_2ClCH_2Cl typically showed higher levels at night at Sites 1

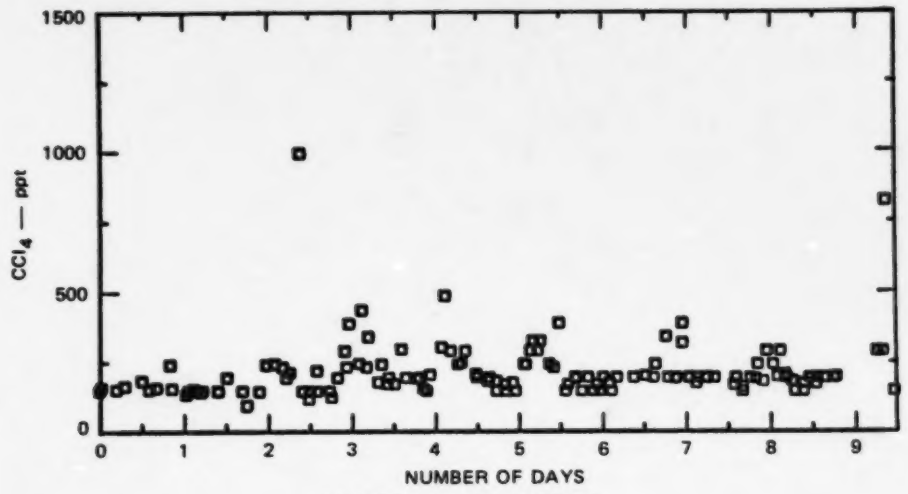


(a) SITE 1 — LOS ANGELES

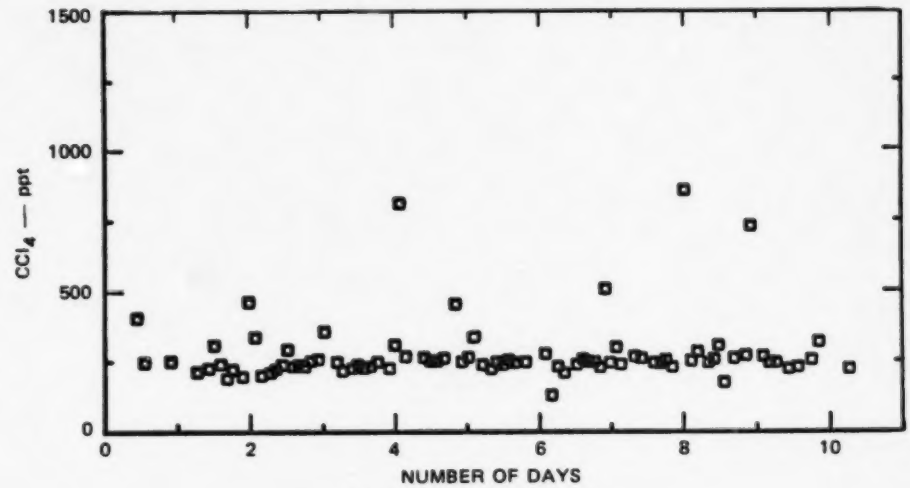


(b) SITE 2 — PHOENIX

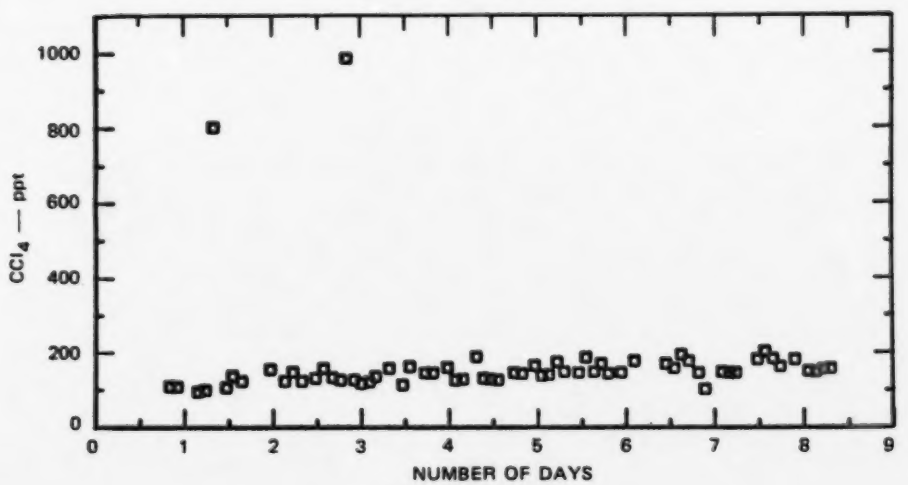
Figure 14. Average diurnal variation of chloroform.



(a) SITE 1 — LOS ANGELES



(b) SITE 2 — PHOENIX



(c) SITE 3 — OAKLAND

Figure 15. Concentration levels of carbon tetrachloride.

TABLE 13. PRODUCTION, EMISSIONS, AND USAGES OF IMPORTANT HALOETHANES.

Compound	Source*	U.S. Production (million metric tons)	Emissions (%)	Usage and Remarks
CH_2ClCH_2Cl	A	5.8 (1978)	≈2	87% used for vinyl chloride monomer synthesis; also used for the production of C_2HCl_3, C_2Cl_4, CH_3CCl_3, CH_2CCl_2; about 0.4 million tons per year used for lead scavenging in automobiles
CH_2BrCH_2Br	A	0.1 (1976)	5–25	Major lead scavenger; also used as a fumigant
CH_3CCl_3	A	0.3 (1977)	≈95	70% of production used for metal cleaning; most other applications also result in direct release

*A = anthropogenic.

Source: A.D. Little (1975); Singh et al. (1979)

and 2. The highest levels in Oakland were in the late afternoon, suggesting the impact of transport from upwind sources. Figure 16 shows average diurnal variation of CH_2ClCH_2Cl at Site 2 (Phoenix). Since an average loss rate of less than 2 percent per day is estimated for CH_2ClCH_2Cl (Table 9) the daytime minimums should not be attributed to chemical loss.

1,2 Dibromoethane (CH_2BrCH_2Br)—1,2 Dibromoethane is a commonly used gasoline additive that finds its way into the atmosphere from mostly evaporative losses. It is also sometimes used as a fumigant. It is expected to be toxic in a manner similar to CH_2ClCH_2Cl. The concentration levels of CH_2BrCH_2Br were found to be generally quite low and maximum concentration did not exceed 0.2 ppb. The average concentration levels of 0.03, 0.04, and 0.02 ppb were measured at Sites 1, 2, and 3 respectively. The lowest levels of 2 to 5 ppt are typical of expected ground level concentrations in unpolluted environments (Singh et al., 1979). Daily average dosages of 6, 7, and 3 μg/day are calculated for Sites 1, 2, and 3 respectively. Figure 17 shows the average diurnal variation of CH_2BrCH_2Br at all three sites and is typical of an automobile-source pollutant. CH_2BrCH_2Br is relatively unreactive, and a daily chemical loss rate of about 2 percent per day (Table 9) is expected.

1,1,1 Trichloroethane (CH_3CCl_3)—Like CH_2Cl_2, CH_3CCl_3 is another large volume chemical that is commonly used as a degreasing solvent (Singh et al., 1979; Farber, 1979). Nearly all of the CH_3CCl_3 produced is eventually released to the atmosphere. No natural sources of CH_3CCl_3 are known or suspected. CH_3CCl_3 is suspected to be mutagenic although considerable disagreement on its mutagenicity and carcinogenic potential persists (Farber, 1979; Lapp et al., 1979). Average concentrations of 1.0, 0.8, and 0.3 ppb were measured at Sites 1, 2, and 3 respectively. Highest concentrations of 5.1, 2.8, and 1.0 ppb were measured at these three

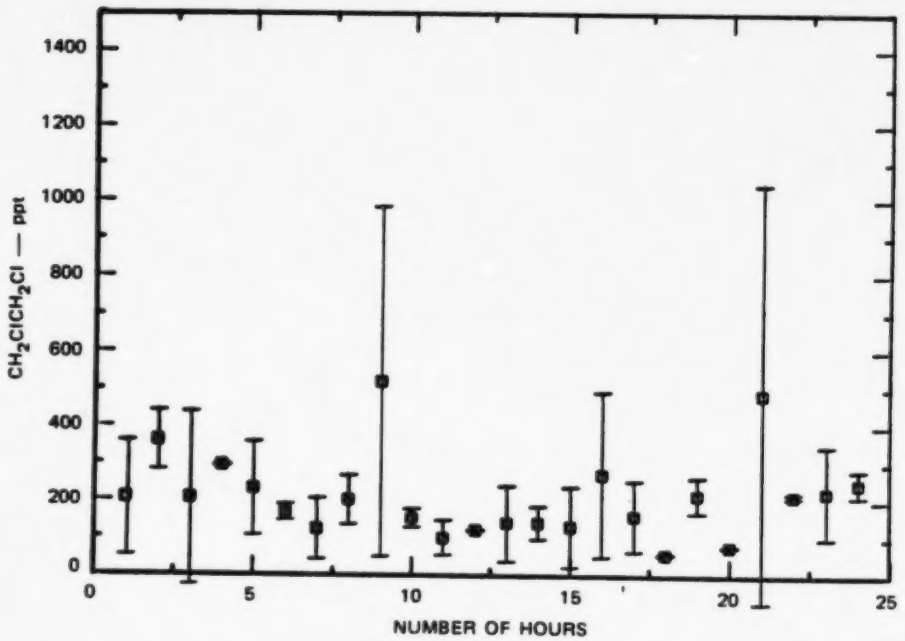


Figure 16. Average diurnal variation of 1,2 dichloroethane at Phoenix — Site 2.

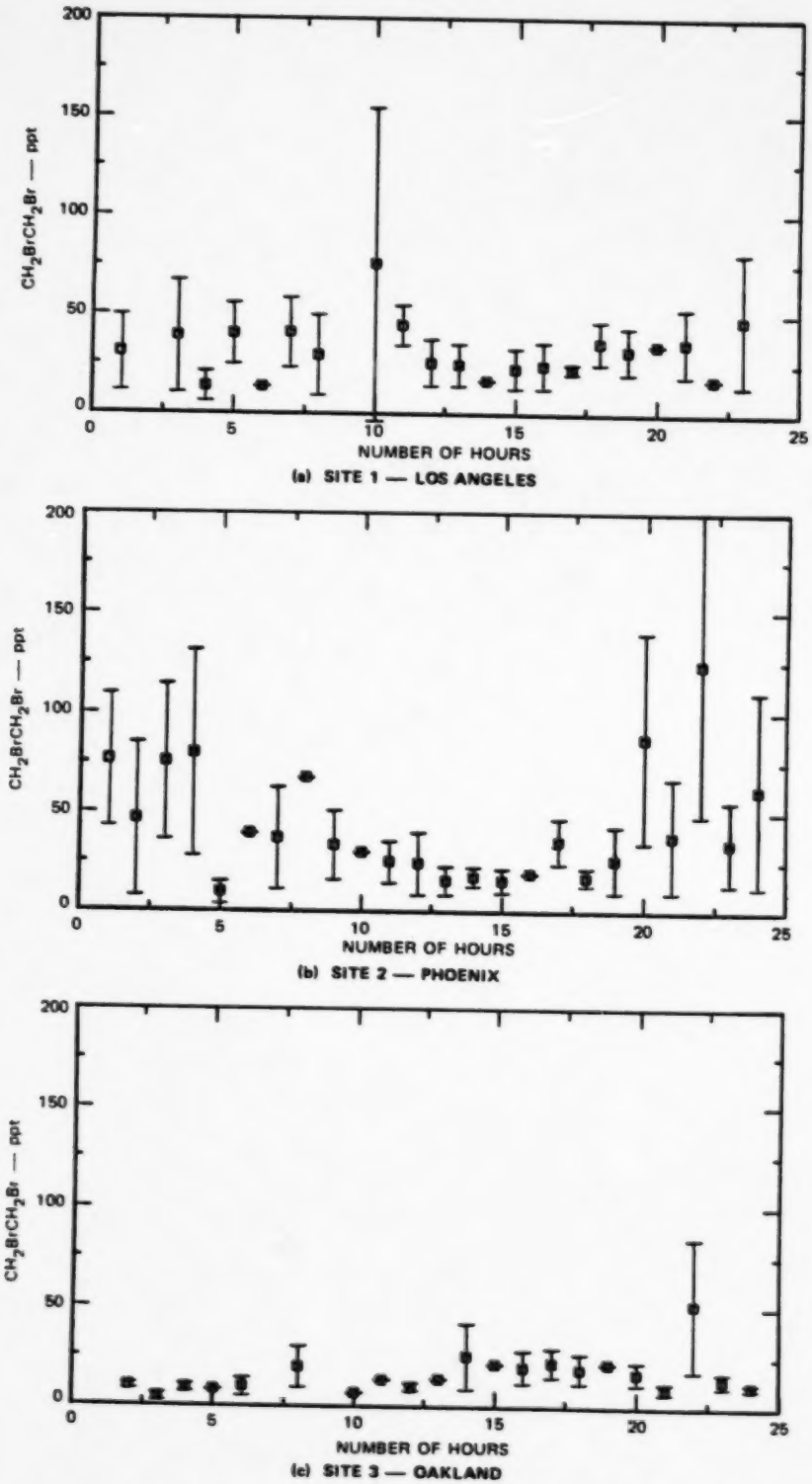


Figure 17. Average diurnal variation of 1,2 dibromoethane.

sites respectively. The lowest concentrations measured were between 1 to 2 times the background concentration of about 140 ppt expected at these latitudes (Singh et al., 1979). We calculate average daily exposures of 133, 116, and 38 μg/day for Sites 1, 2, and 3 respectively. This should be compared with the average exposure of 18 μg/day in a locally unpolluted environment.

Figure 18 shows a typical average diurnal profile for CH_3CCl_3 at Sites 1 and 2. Somewhat elevated early-morning levels are observed at both sites. A late-evening minimum is also observed, probably a result of reduced emissions of CH_3CCl_3. At Site 3, the average diurnal variability in CH_3CCl_3 was less distinct, the actual concentration data is presented for Site 3. On several days (Figure 19) higher morning or late-evening levels are indicated. CH_3CCl_3, for all practical purposes, is an inert pollutant with a residence time that can be measured in years (Singh et al., 1979).

1,1,2 Trichloroethane ($CH_2ClCHCl_2$)—The average concentration of this chemical did not exceed 16 ppt at any of the sites. The highest concentration of 46 ppt was measured at Site 1. While the chemical was measured ubiquitously at Sites 1 and 3, its concentration was above 1 ppt only 39 percent of the time at Site 2 (Table10). The lowest concentration at Sites 1 and 3 was 4 ppt while it was less than 1 ppt at Site 2. An average daily dose of 1 μg/day is calculated for each of the three sites. Figure 20 shows the diurnal variability at Sites 1 and 3.

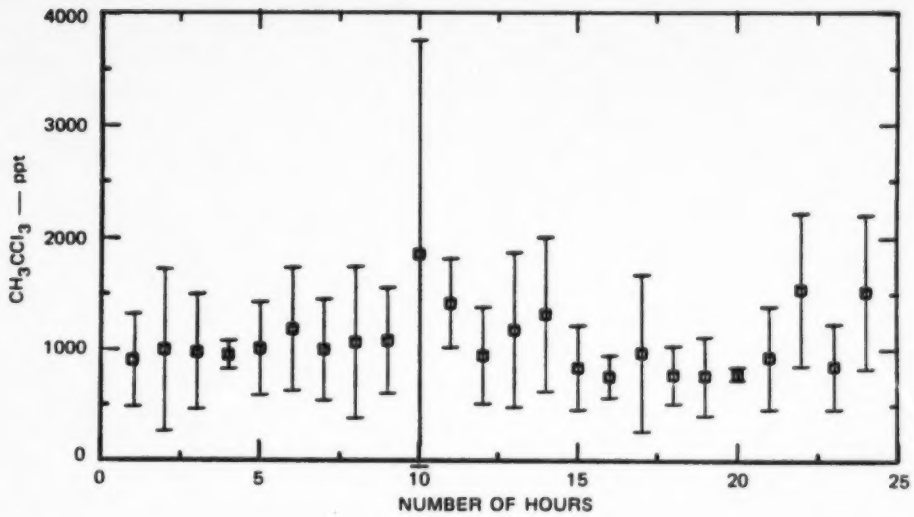
1,1,1,2 Tetrachloroethane (CH_2ClCCl_3)—As shown in Table10, the concentration of this chemical never exceeded 17 ppt. Average concentrations of 4, 9, and 4 ppt were measured at Sites 1, 2, and 3 respectively. This compound was not detectable at all times; the measurement frequency was 50, 10, and 97 percent at Site 1, 2, and 3 respectively. The average daily dose is calculated to be less than 1 μg/day for each site. As indicated in Table 9, tetrachloroethanes are highly unreactive.

1,1,2,2 Tetrachloroethane ($CHCl_2CHCl_2$)—Of the two isomers, this symmetric isomer was the more abundant. Its concentration did not exceed 100 ppt at any of the sites. The average concentration of $CHCl_2CHCl_2$ was measured to be 17, 17, and 7 ppt at Sites 1, 2, and 3 respectively. At Site 2, the levels were below 1 ppt about 20 percent of the time. The average daily dosage is calculated to be 3, 2, and 1 μg/day for Sites 1, 2, and 3 respectively. Figure 21 shows the average measured diurnal variation for Los Angeles. For all practical purposes $CHCl_2CHCl_2$ can be considered essentially inert.

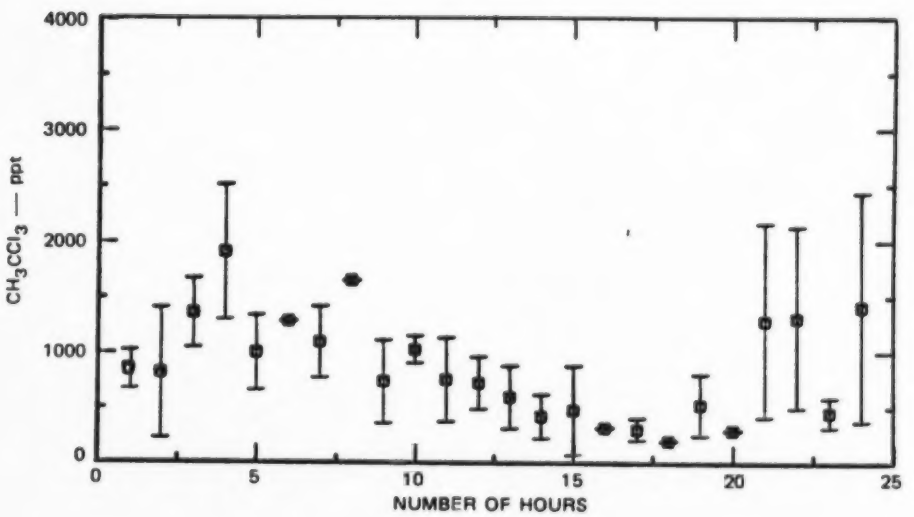
3. *Chloroethylenes*

Table 9 shows that a total of four chloroethylenes were measured. Data is presented only for three of these since, as stated earlier, we are unconvinced of the true identity of cis-CHClCHCl. Table 14 lists the selected large-volume chloroethylenes, their sources, production, and uses. None of the chloroethylenes are known to have any natural sources. These section discusses the measured chloroethylenes, which are considered quite toxic, in more detail.

Vinyledene Chloride (CH_2CCl_2)—Vinyledene chloride was measured at an average concentration of only 5, 30, and 13 ppt at Sites 1, 2, and 3 respectively. A maximum concentration of 160 ppt was measured at Site 2. Based on our data, daily average doses of 0.4, 2.5, and 1.1 μg/day can be calculated. As is clear from Table 9, CH_2CCl_2 is highly reactive and a 30 percent loss per day can occur as a result of chemistry alone. In the absence of unusually large sources, it is not possible for CH_2CCl_2 to build up in the atmosphere because of a very short lifetime of about 3 days.



(a) SITE 1 — LOS ANGELES



(b) SITE 2 — PHOENIX

Figure 18. Average diurnal variation of 1,1,1 trichloroethane.

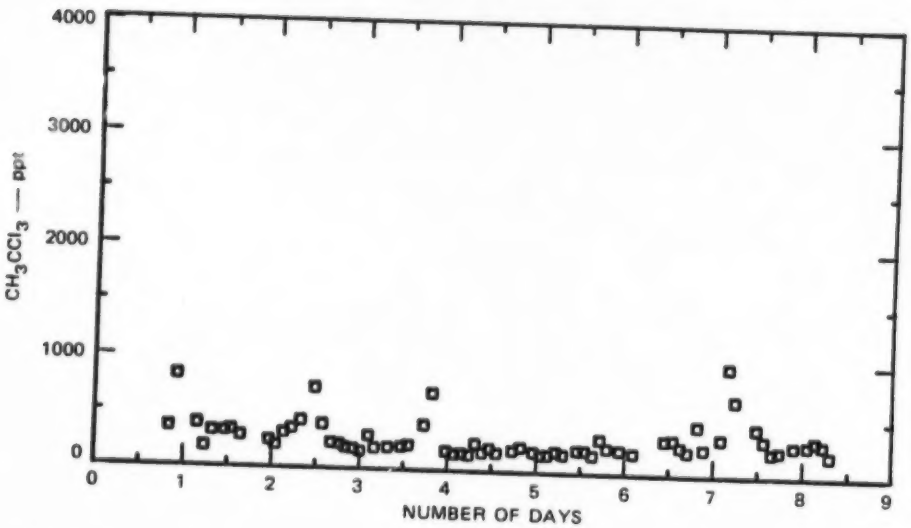
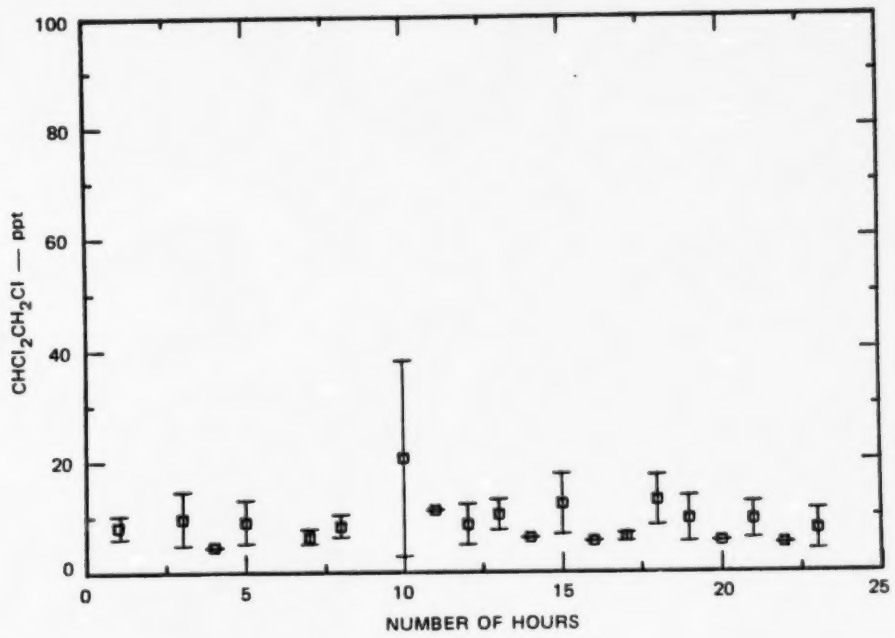
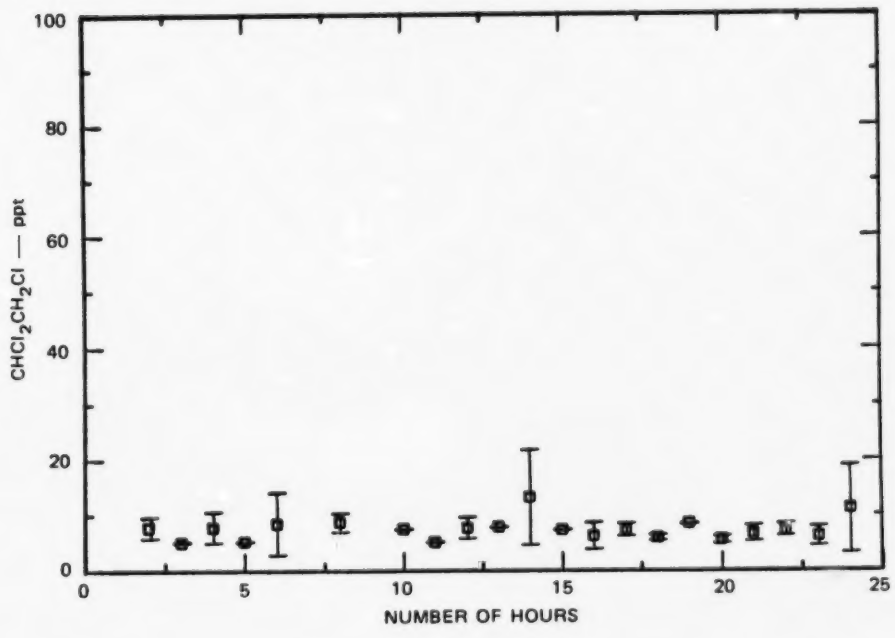


Figure 19. Atmospheric concentration of 1,1,1 trichloroethane at Oakland — Site 3.



(a) SITE 1 — LOS ANGELES



(b) SITE 3 — OAKLAND

Figure 20. Average diurnal variation of 1,1,2 trichloroethane.

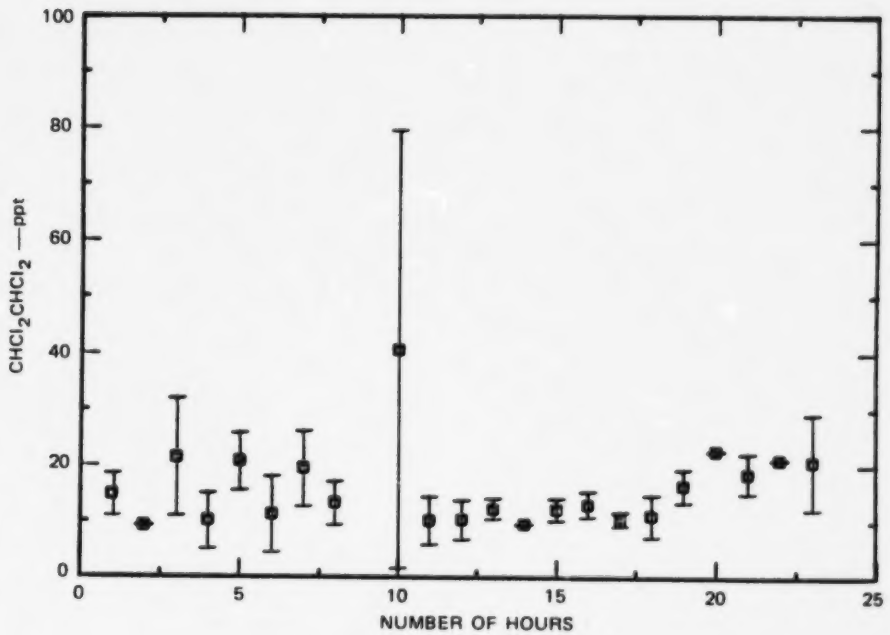


Figure 21. Average diurnal variation of 1,1,2,2 tetrachloroethane at Los Angeles — Site 1.

TABLE 14. PRODUCTION, EMISSION AND USAGES OF IMPORTANT CHLOROETHYLENES.

Compound	Source*	U.S. Production (million metric tons)	Emissions(%)	Usage and Remarks
$CH = CHCl$	A	2.5 (1974)	2 - 5	Used for polymer synthesis
$CH_2 = CCl_2$	A	0.2 (1974)	2 - 5	Used for polymer synthesis
$CHCl = CCl_2$	A	0.14 (1977)	>90	70 - 80% used for metal cleaning
$CCl_2 = CCl_2$	A	0.30 (1977)	>90	60% used for dry cleaning and textile processing, another 15% used for metal cleaning

*A = anthropogenic.
Source: A.D. Little (1975); Singh et al. (1979)

Trichloroethylene ($CHClCCl_2$)—Trichloroethylene is another high-volume solvent that is emitted to the atmosphere in large quantities. It is also a suspected carcinogen (CEN, 1975). During our field experiments C_2HCl_3 concentrations as high as 3.1 ppb were measured. The average concentrations as measured at Sites 1, 2, and 3 were 0.4, 0.5, and 0.2 ppb respectively. The lowest measured levels were 1 to 3 times the expected ground-level background concentration of about 10 to 15 ppt (Singh et al., 1979). The average daily dosage is calculated to be 58, 76, and 20 μg/day at Sites 1, 2, and 3 respectively.

C_2HCl_3, unlike chloroethanes, is highly reactive and a residence time of about 5 days is estimated (Table 9). Thus about 20 percent of C_2HCl_3 can be chemically decomposed every day. The diurnal variation of C_2HCl_3 is best demonstrated at Site 2, shown in Figure 22. The same pattern is observed at Site 1 but is much less pronounced. At Site 3, a second afternoon maxima appears.

Tetrachloroethylene (CCl_2CCl_2)—The toxicity of C_2Cl_4 is currently a matter of considerable debate, but there is evidence that it may be carcinogenic (Albert, 1978; Greenberg and Parker, 1979; Altshuller, 1979). C_2Cl_4 is significantly less reactive than C_2HCl_3, and a daily chemical loss rate of less than 2 percent is expected (Table 9). A maximum C_2Cl_4 concentration of 4 ppb was measured: Average concentrations of 1.5, 1.0, and 0.3 ppb were measured at Sites 1, 2, and 3 respectively. The lowest measured concentrations were 1 to 4 times the measured background levels of about 45 ppt (Singh et al., 1979). The daily average dose of 236, 173, and 46 μg/day was calculated for Sites 1, 2, and 3 respectively. These should be compared with an estimated dose of about 7 μg/day for a clean background environment.

The diurnal variation of C_2Cl_4 was once again strongest at Site 2. It shows a pronounced maximum in the early-morning hours and a minimum in the late afternoon. The diurnal behavior at Los Angeles (Site 1) showed an essentially uniform diurnal profile, while an afternoon maximum is observed in Oakland. Most likely a result of transport from upwind sources. Figure 23 shows the average C_2Cl_4 diurnal variation for Site 2 and 3.

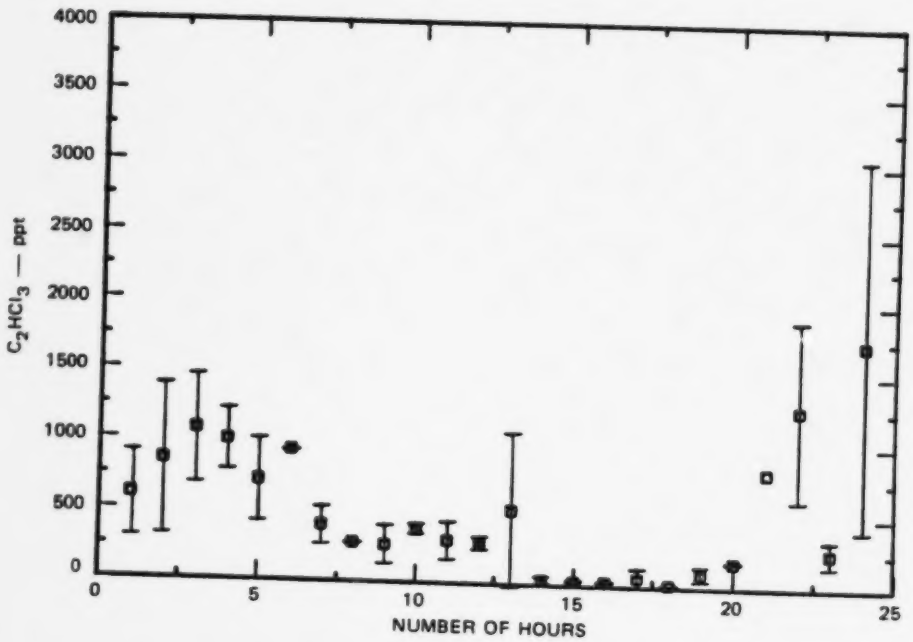
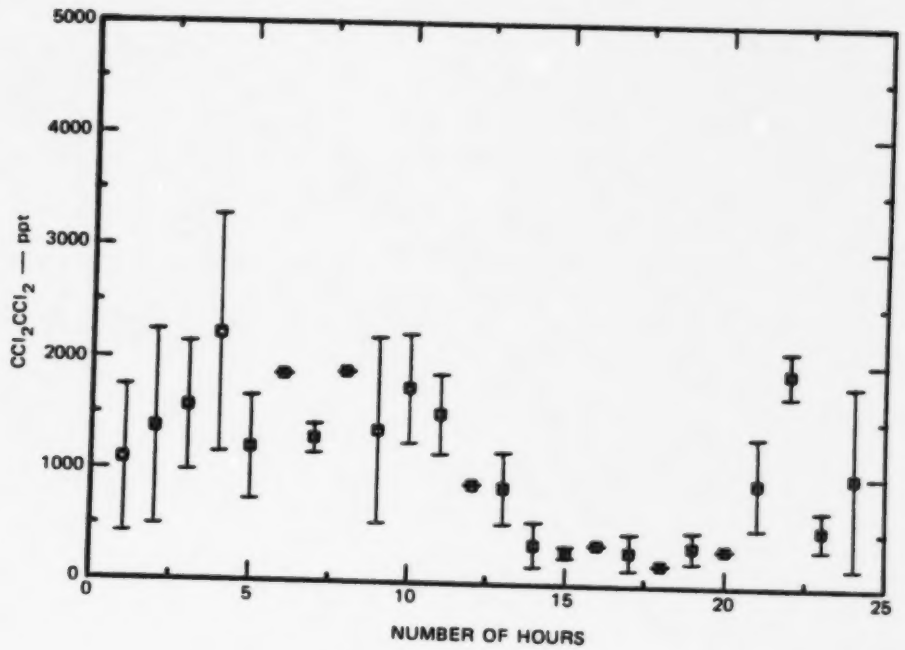
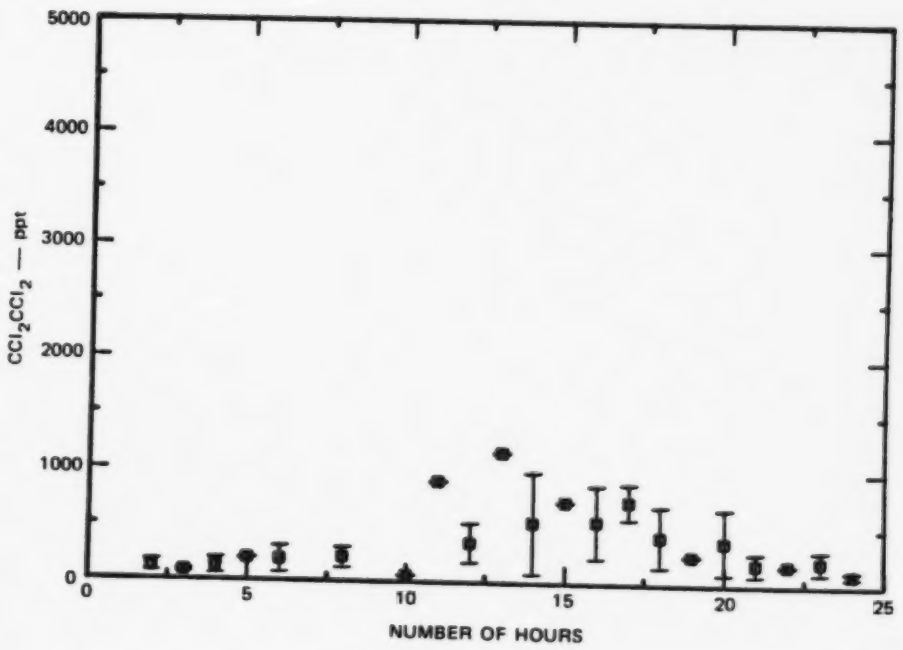


Figure 22. Average diurnal variation of trichloroethylene at Phoenix — Site 2.



(a) SITE 2 — PHOENIX



(b) SITE 3 — OAKLAND

Figure 23. Average diurnal variation of tetrachloroethylene.

4. *Chlorobenzenes*

Monochlorobenzene, o-dichlorobenzene, m-dichlorobenzene, and 1,2,4 trichlorobenzene were measured. P-dichlorobenzene could not be measured because of interferences from other unknown species. Table 15 briefly describes the production, estimated emissions, and use patterns of the dominant chlorobenzenes. While monochlorobenzene and dichlorobenzenes are the dominant species, smaller amounts of trichlorobenzenes (13,000 tons) and tetrachlorobenzenes (8,000 tons) are also produced. It is possible that large quantities of chlorobenzenes are released into the environment.

Monochlorobenzene (C_6H_5Cl)—Monochlorobenzene data was discarded because a GC artifact made it difficult to quantify C_6H_5Cl levels. (In many cases, the artifact could be easily distinguished from the C_6H_5Cl peak. The GC-EC response to C_6H_5Cl is quite poor.) More accurate data on C_6H_5Cl will be acquired in the second year of this project.

From a semiquantitative analysis of data, it appears that the C_6H_5Cl levels typically did not exceed 0.5 ppb. Levels were also higher at Sites 1 and 2 when compared with Site 3: We estimate that the average C_6H_5Cl concentrations at Sites 1 and 2 were about 0.2 ppb, and roughly half that at Site 3. An estimated average daily dose of 21, 21, and 10 μg/day is calculated for Sites 1, 2, and 3. C_6H_5Cl is moderately reactive and about 4 percent loss per day can be expected as a result of chemistry alone (Table 9).

Ortho and Meta Dichlorobenzenes (o-$C_6H_4Cl_2$ and m-$C_6H_4Cl_2$)—Both ortho and meta isomers were measured at Sites 1, 2, and 3 and were found to be present 100 percent of the time (Table 10). An average o-$C_6H_4Cl_2$ concentration of 0.13, 0.23, and 0.04 ppb was measured at

TABLE 15. PRODUCTION, EMISSIONS, AND USAGE OF IMPORTANT CHLOROBENZENES.

Compound	Source*	U.S. Production (million metric tons)	Emissions (%)	Usages and Remarks
C_6H_5Cl	A	0.17 (1976)	>50	50% used in solvent applications, remainder in the production of nitrobenzene, DDT, diphenyl oxide
o-$C_6H_4Cl_2$	A	0.04 (1976)	>25	About 25% of production used in solvent applications
p-$C_6H_4Cl_2$	A	0.03 (1976)	No data	90% of production used for space deodorizing and moth control
1,2,4 $C_6H_3Cl_3$	A	0.01 (1973)	No data	70% used as a dye carrier and a herbicide intermediate

*A = anthropogenic.

Source: Ware and West (1977); CIS (1979)

Sites 1, 2, and 3 respectively. The maximum o-$C_6H_4Cl_2$ concentration was measured to be 2.4 ppb, however this happened only once: A more typical maximum was 1.5 ppb. The daily average dosage at these three sites respectively is calculated to be 19, 28, and 5 μg/day.

M-$C_6H_4Cl_2$, somewhat less abundant when compared with the o-$C_6H_4Cl_2$ at Sites 1 and 2, was present at an average concentration of 0.08 and 0.09 ppb respectively. At Site 3, the average concentrations of the m-$C_6H_4Cl_2$ isomer was 0.07 ppb, somewhat higher than the o-$C_6H_4Cl_2$ concentration. The highest m-$C_6H_4Cl_2$ concentration did not exceed 0.3 ppb. The m-$C_6H_4Cl_2$ dosage at Site 3 is calculated to be 9 μg/day.

As estimated in Table 9, residence times of $C_6H_4Cl_2$ (isomers) are long and daily losses resulting from chemistry are expected to be less than 1 percent per day. Figure 24 shows the average diurnal variation observed for m- and o-$C_6H_4Cl_2$ at Phoenix. The diurnal variation at Site 1 was very similar but somewhat less pronounced when compared to Site 2. A mid-afternoon maximum observed at Site 3 appears to be a typical feature of this site.

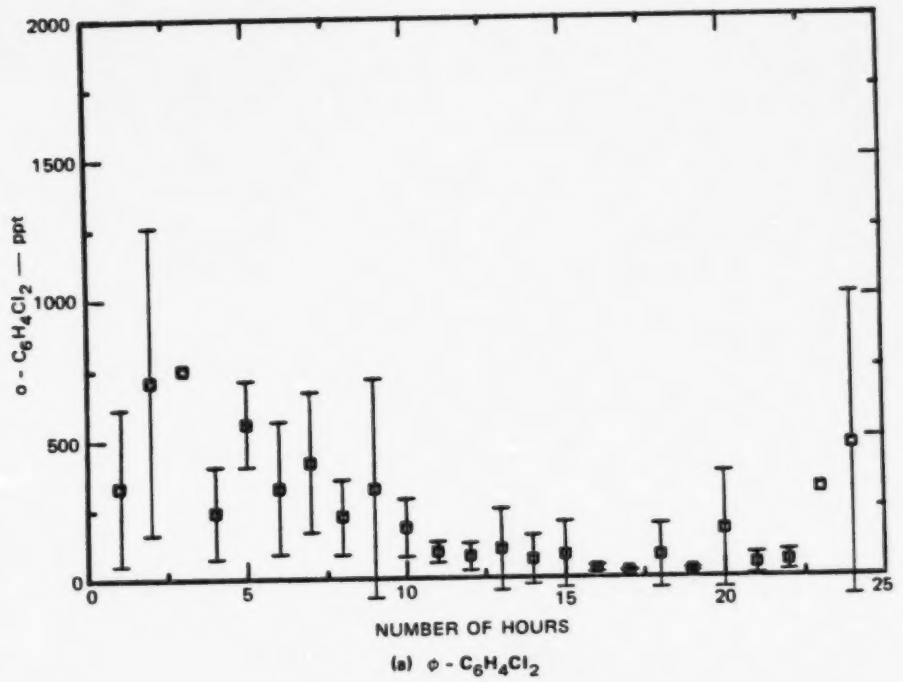
1,2,4-Trichlorobenzene—As is clear from Table 10, 1,2,4-$C_6H_5Cl_3$ was present at relatively low concentration levels, and a maximum concentration of 0.34 ppb was measured. The average concentrations at Sites 1, 2, and 3 were 0.07, 0.03, and 0.03 ppb respectively. An average daily dose of 12, 5, and 6 μg/day respectively is calculated for Sites 1, 2, and 3. For all practical purposes $C_6H_5Cl_3$ (isomers) would be inert in the urban environment and a loss resulting from chemistry of less than 0.1 percent per day would occur (Table 9). The average diurnal variation at Phoenix is shown in Figure 25. At Site 1, the diurnal variation was similar but less pronounced. At the Oakland site, somewhat higher levels during late morning and late evening were evident.

5. *Aromatic Hydrocarbons*

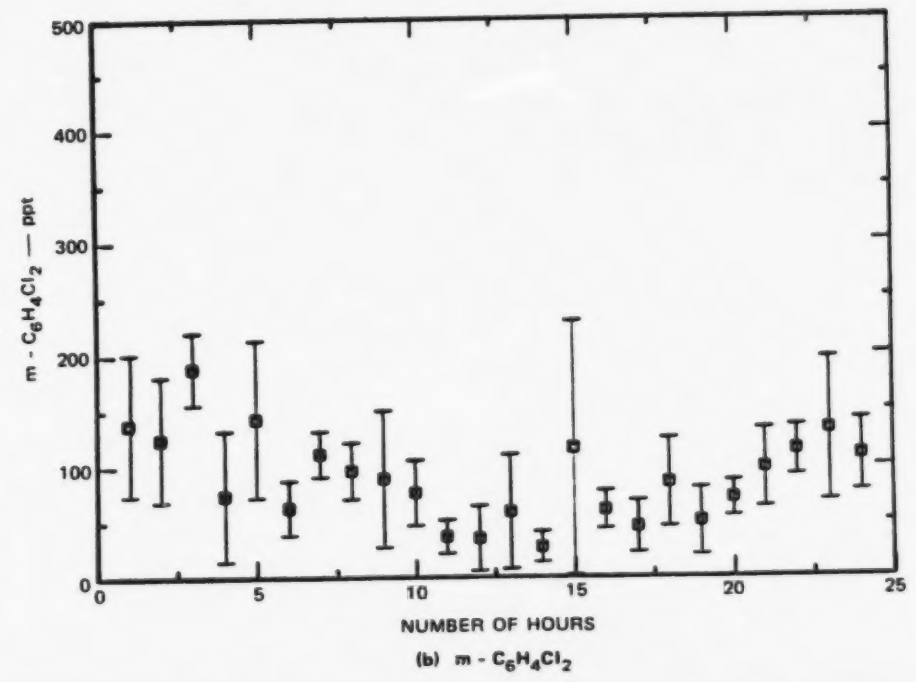
Aromatic hydrocarbons are produced and released in significant quantities. Production of benzene, toluene, and xylenes for the United States is currently estimated to be 3.5, 2.5, and 3.8 million tons per year. Over 95 percent of these aromatics are used as chemical processing intermediates. A major fraction of atmospheric release comes from automobiles; the aromatic content of gasoline has increased over the last five years, resulting in increased emissions. Benzene has received a great deal of attention because of its carcinogenic potential (Albert, 1977). Toluene and xylenes are also suspect as carcinogens, although detailed toxicity studies are not complete (Federal Register, 1977).

A number of aromatic hydrocarbons were measured in this study. Because of their structural similarity they can all be considered potentially hazardous. As summarized in Table 11, the exposure to this group of chemicals is the highest; daily doses of 2,700, 2,228, and 710 μg/day were determined for Sites 1, 2, and 3 respectively.

Benzene (C_6H_6)—Average C_6H_6 concentrations of 6.0, 4.7, and 1.6 ppb and maximum concentrations of 28, 60, and 5 ppb were measured at Sites 1, 2, and 3 respectively. At all sites, the lowest concentrations were below 1 ppb. The average daily dose is calculated to be 424, 350, and 105 μg/day at Sites 1, 2, and 3 respectively. Benzene could be measured 100 percent of the time at all three sites. It is evident from Table 9 that C_6H_6 is quite reactive, and an 11 percent per day loss rate as a result of chemical reactions alone is possible.



(a) o - $C_6H_4Cl_2$



(b) m - $C_6H_4Cl_2$

Figure 24. Average diurnal variation of ortho and meta dichlorobenzene at Phoenix — Site 2.

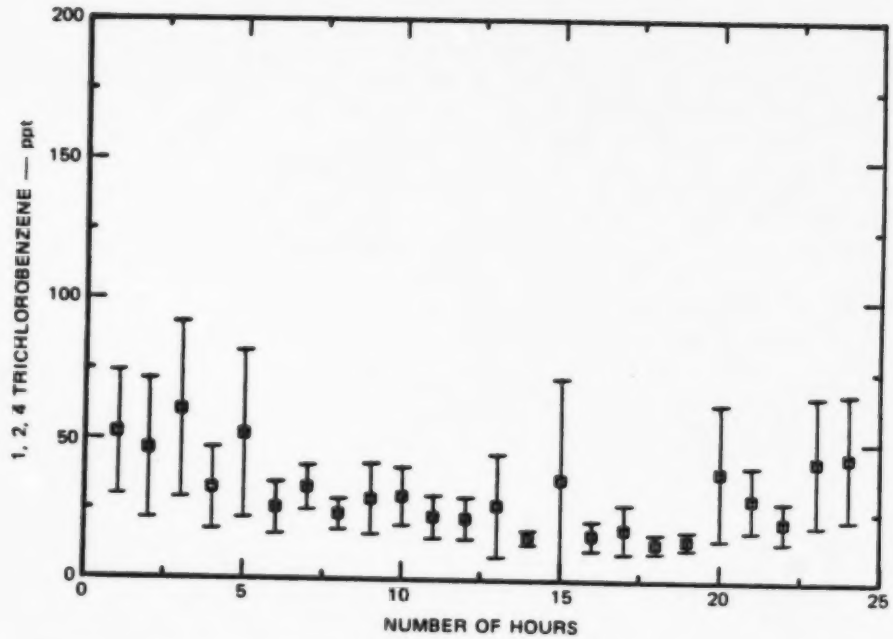


Figure 25. Average diurnal variation of 1,2,4 trichlorobenzene at Phoenix — Site 2.

The mean diurnal variation of benzene for Sites 1, 2, and 3 is shown in Figure 26. All three sites show an early morning cycle that coincides with local vehicular activity. The nighttime C_6H_6 levels are typically higher at Sites 1 and 2, probably a result of shallow nocturnal inversions. As expected, the diurnal cycle is most pronounced at Site 2 with very low afternoon levels. At Site 3, the highest values are observed in the afternoon.

Toluene ($C_6H_5CH_3$)—Toluene was typically more abundant than benzene by about a factor of 2 at all three sites. The average toluene concentration was measured to be 12, 9, and 3 ppb, resulting in daily average doses of 1,028, 705, and 261 μg/day at Sites 1, 2, and 3, respectively. The highest toluene concentration of 53 ppb was measured at Site 1: The lowest concentrations were less than 1 ppb. Toluene is significantly more reactive than benzene, and an estimated (Table 9) chemical loss rate of 41 percent per day is possible. The high reactivity and the high abundance of toluene point to very large sources. The diurnal behavior of toluene (very similar to C_6H_6) is clearly shown in Figure 27 for Sites 1, 2, and 3.

Ethyl Benzene ($C_6H_5C_2H_5$)—Average concentrations of 2.3, 2.0, and 0.6 ppb and daily average dosage of 213, 182, and 59 μg/day were determined for Sites 1, 2, and 3 respectively. The highest concentration of 28 ppb was measured at Site 1: Minimum concentrations were below 0.1 ppb. The reactivity of ethyl benzene is slightly greater than that of toluene and a chemical loss rate of 50 percent per day is estimated (Table 9). The diurnal behavior of ethyl benzene at all three sites is almost identical to that of toluene, pointing to a common source. Figure 28 shows an example of this behavior for Sites 1 and 2.

Meta, Para, and Ortho Xylenes [m,p,o-$C_6H_4(CH_3)_2$]—All three isomers of xylene were measured. M/p-xylenes were measured together, while o-xylene was exclusively separated. It is clear from Table 10 that m/p-xylene abundance was roughly twice that of o-xylene. The highest concentration of 50 ppb for m/p-xylenes and 13 ppb for o-xylene was measured at Site 1.

The average m/p-xylene concentrations of 4.6, 4.2, and 1.5 ppb, resulting in daily dosages of 439, 419, and 151 μg/day, were determined for Sites 1, 2, and 3 respectively. The average o-xylene concentrations for Sites 1, 2, and 3 were 1.9, 1.8, and 0.8 ppb, and the corresponding calculated dosages are 192, 171, and 69 μg/day. Xylenes are highly reactive, and 70 to 90 percent (Table 9) of the isomers may be lost every day as a result of chemistry alone. The diurnal behavior of m/p-xylenes at Sites 1, 2, and 3, shown in Figure 29, is almost identical to that of benzene and toluene. The behavior of o-xylene is completely identical as shown in Figure 30 for Site 1.

4-Ethyl Toluene (4-$C_6H_4CH_3C_2H_5$)—Average concentrations of 1.5, 1.5, and 0.7 ppb were measured at Sites 1, 2, and 3 respectively. The average doses at these sites are calculated to be 175, 170, and 66 μg/day. The highest concentration of 10 ppb was measured at Site 1. The reactivity of 4-ethyl toluene is almost identical to p-xylene (Table 9), and a chemical loss rate of 70 percent per day is possible. The diurnal variation of 4-ethyl toluene is also identical to the xylenes, as shown in Figure 31.

1,2,4 and 1,3,5 Trimethyl Benzenes (*1,2,4 and 1,3,5* $C_6H_3(CH_3)_3$)—Both 1,2,4 and 1,3,5 trimethyl benzenes (TMB) were measured; the former was typically much more abundant than the latter. While 1,2,4 TMB was measured 100 percent of the time, 1,3,5 TMB was undetectable ($<$ 0.04 ppb) about 22 percent of the time at Site 1 and 32 percent of the time at Site 2. (These compounds were very low at Site 3 and were not measured.) Both of these isomers are so reactive that nearly 95 to 100 percent could be depleted by chemical reactions in one day (Table 9).

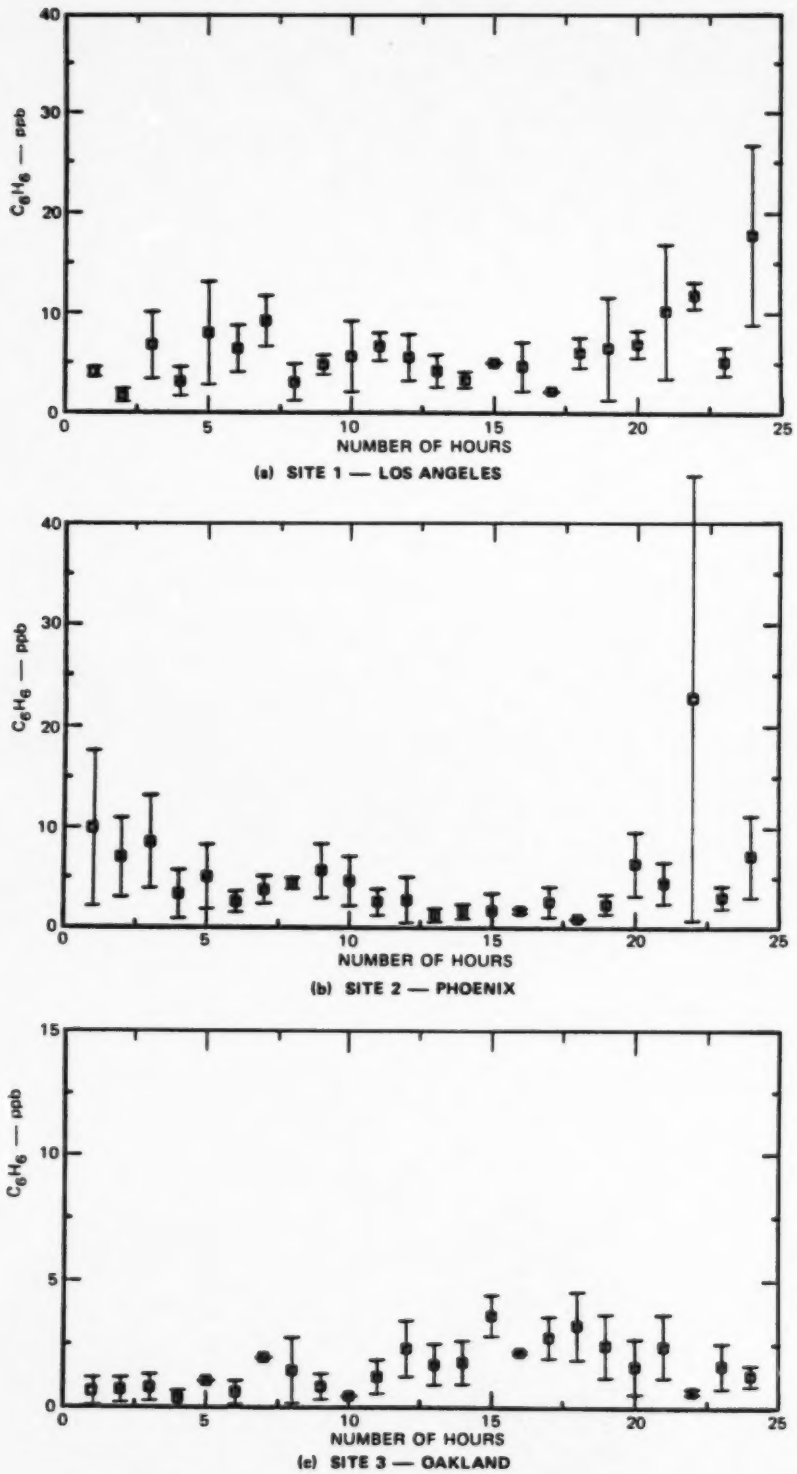


Figure 26. Average diurnal variation of benzene.

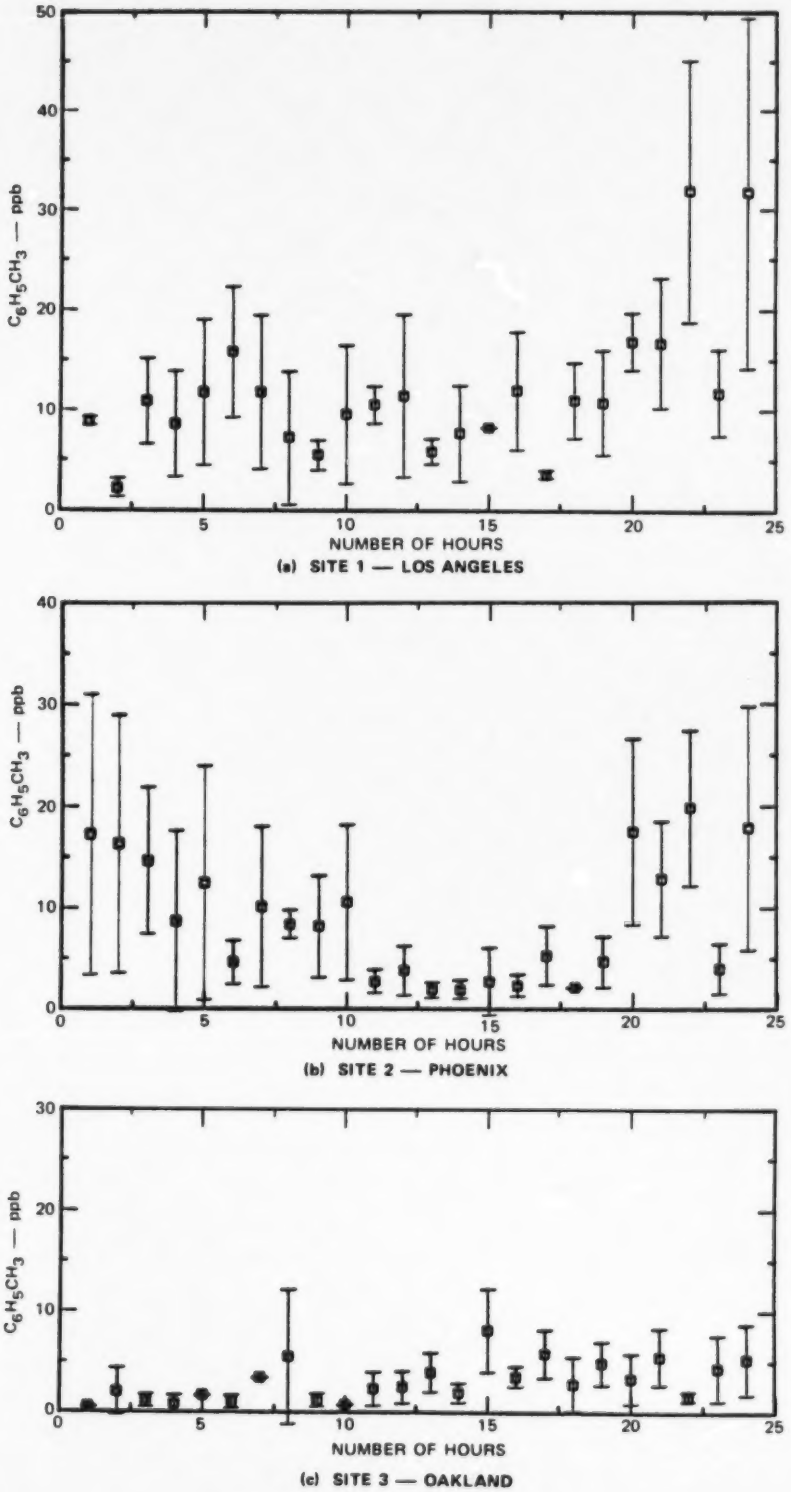
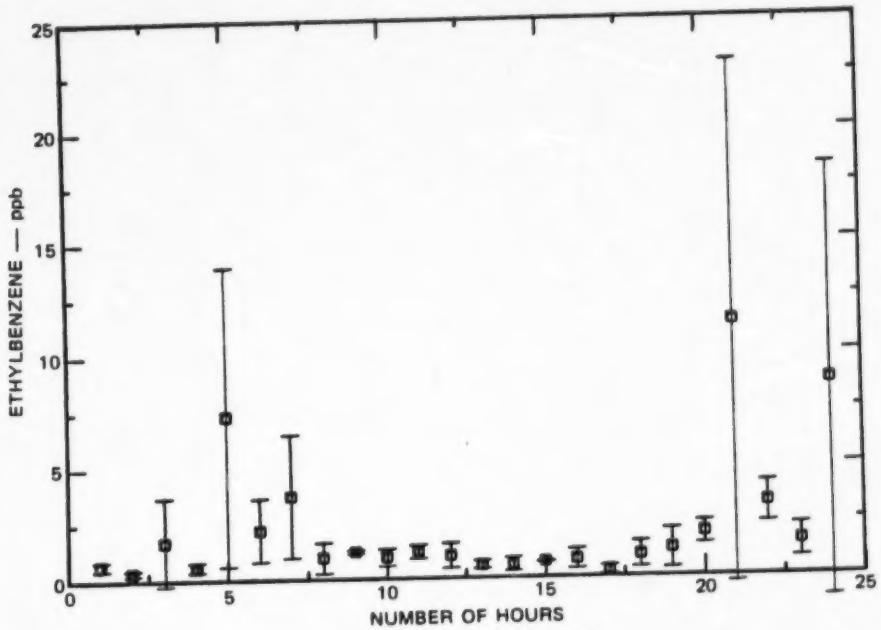
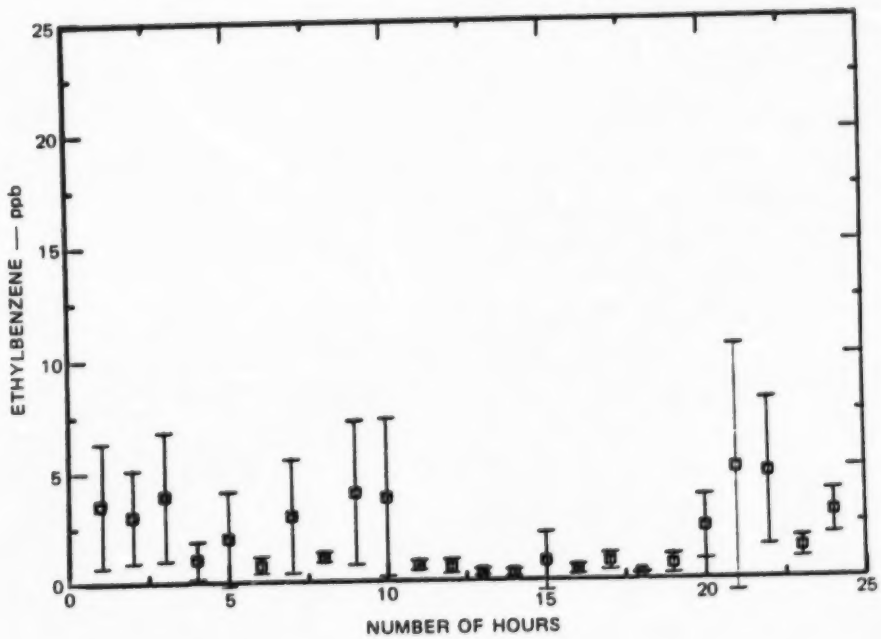


Figure 27. Average diurnal variation of toluene.



(a) SITE 1 — LOS ANGELES



(b) SITE 2 — PHOENIX

Figure 28. Average diurnal variation of ethylbenzene.

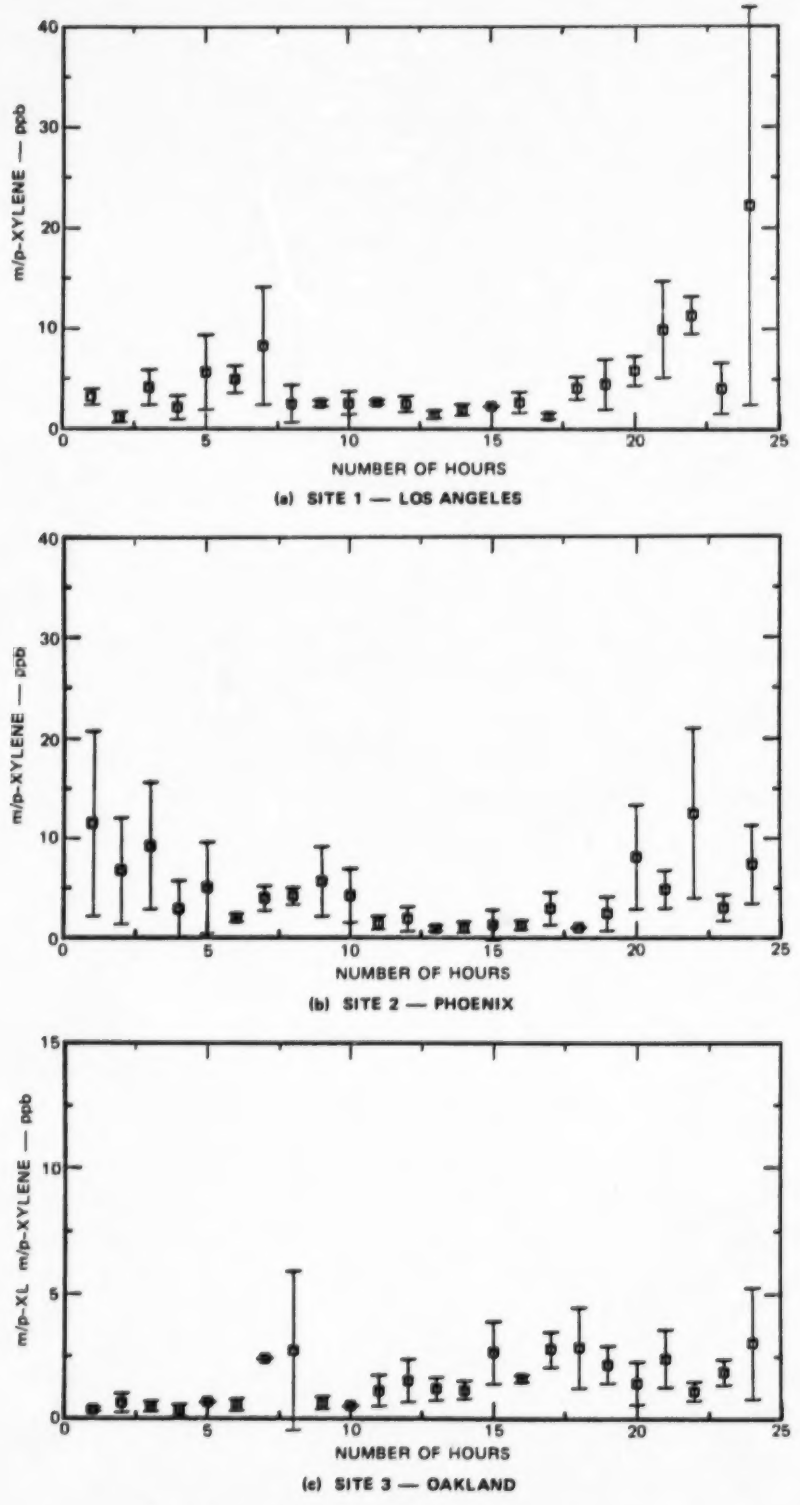


Figure 29. Average diurnal variation of m/p-xylenes.

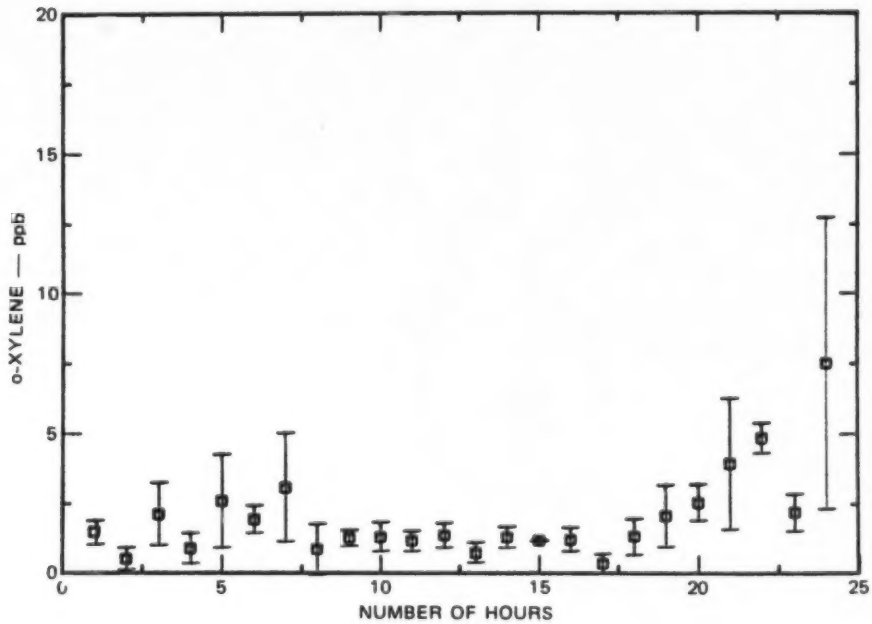


Figure 30. Average diurnal variation of o-xylene at Los Angeles — Site 1.

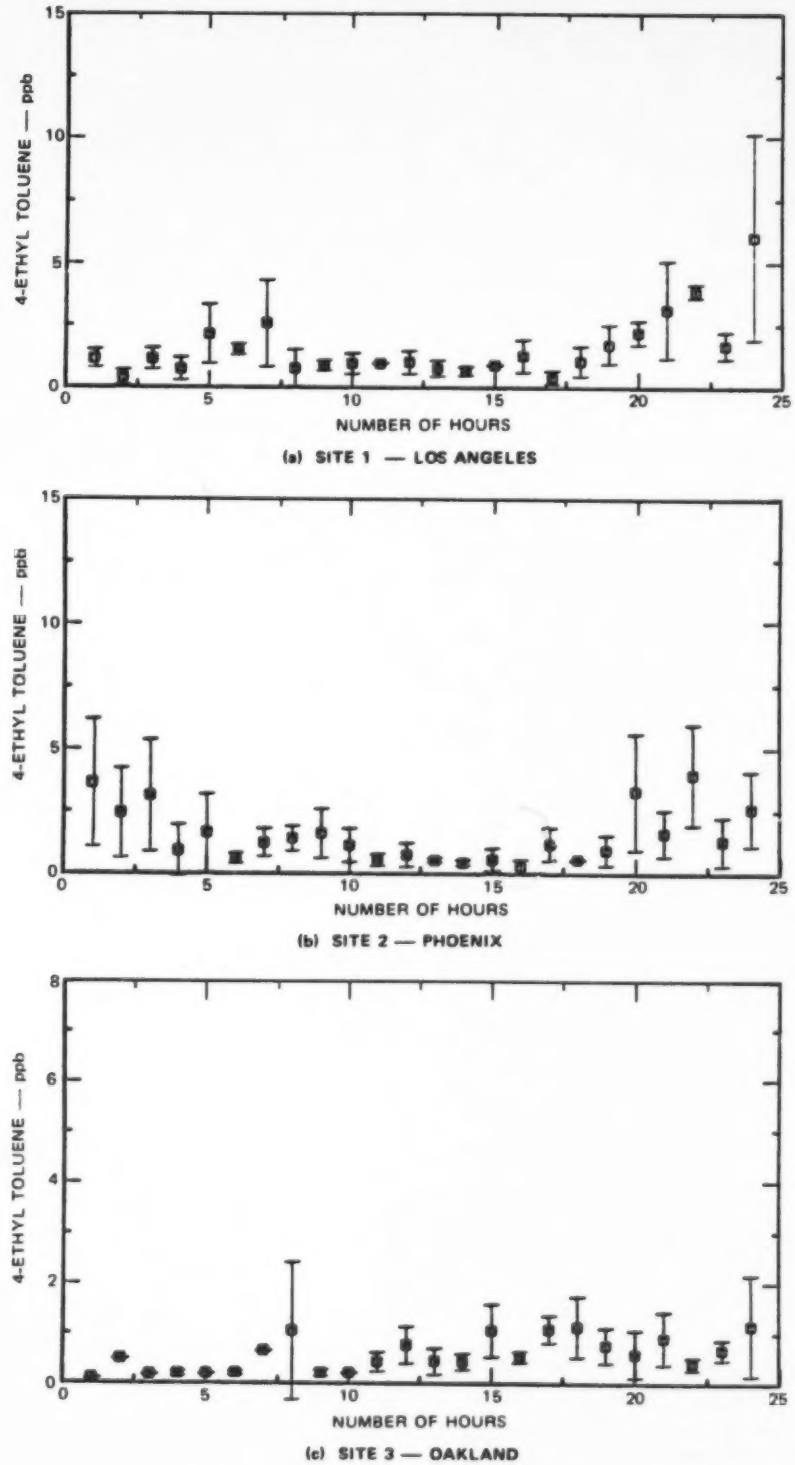

4-ETHYL TOLUENE — ppb
NUMBER OF HOURS
(a) SITE 1 — LOS ANGELES
4-ETHYL TOLUENE — ppb
NUMBER OF HOURS
(b) SITE 2 — PHOENIX
4-ETHYL TOLUENE — ppb
NUMBER OF HOURS
(c) SITE 3 — OAKLAND

Figure 31. Average diurnal variation of 4-ethyl toluene.

Average concentrations of 1.9 and 1.7 ppb, resulting in daily dosages of 34 and 31 μg/day for Sites 1 and 2, respectively, could be determined for 1,2,4 TMB. The highest 1,2,4 TMB and 1,3,5 TMB concentrations were measured in Los Angeles (Site 1): 13, and 5 ppb, respectively. The average concentration for 1,3,5 TMB was 0.4 ppb at both Sites 1 and 2, resulting in daily dosages of 34 and 31 μg/day, respectively. Figure 32 clearly shows the diurnal variation of 1,2,4 TMB at Sites 1 and 2. The diurnal behavior of 1,3,5 TMB was identical to 1,2,4 TMB at both sites.

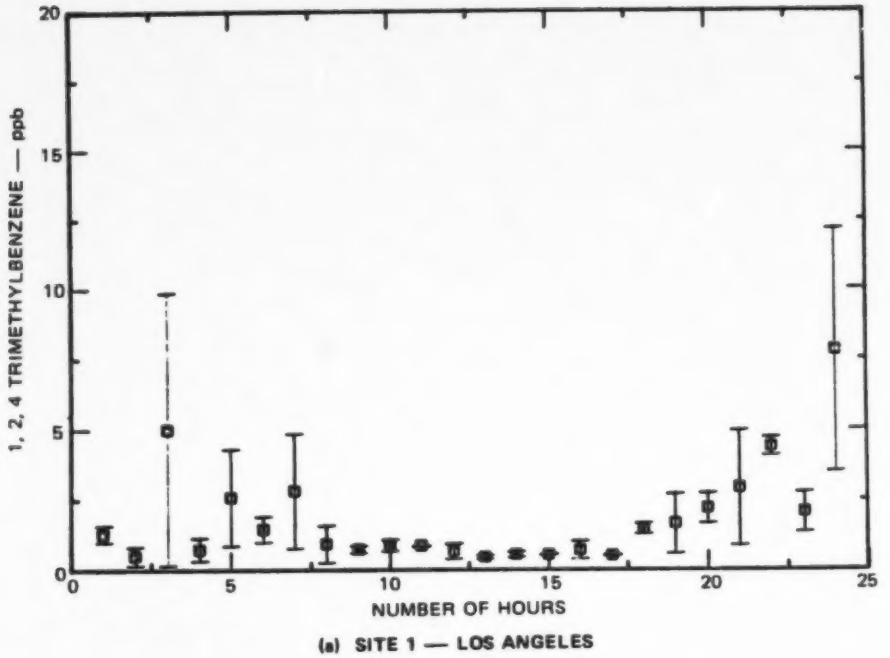
6. *Oxygenated Secondary Species*

The three species in this category, phosgene, peroxyacetyl nitrate (PAN), and polypropionyl nitrate (PPN), are discussed in the sections below.

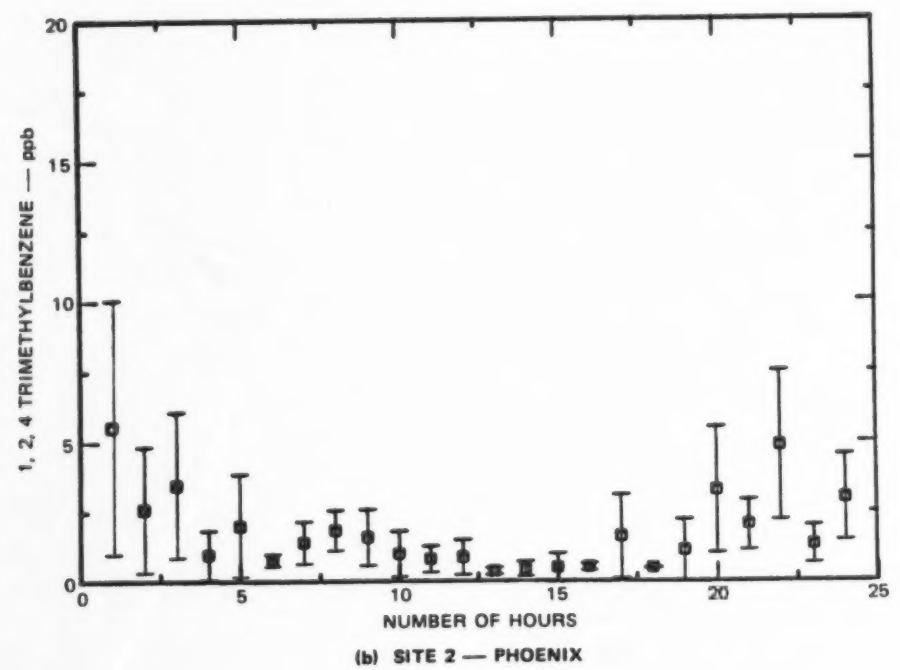
Phosgene ($COCl_2$)—Because of instrument malfunction, phosgene could not be measured as Sites 1 and 2. It was possible to obtain limited data at Site 3, where phosgene was measured at an average concentration of 50 ppt. A daily dose of 5 μg/day is calculated. Data was insufficient to study the diurnal behavior of phosgene; the fate of phosgene has already been discussed in the literature (Singh, 1976).

Peroxyacetyl Nitrate ($CH_3COOONO_2$)—The photochemical synthesis of peroxyacetyl nitrate (PAN) in polluted atmospheres containing hydrocarbon and NO_x has been known for over two decades: Photochemically produced secondary pollutants are known to be hazardous. Levels of PAN as high as 17, 4, and 2 ppb were measured at Sites 1, 2, and 3. Average PAN concentrations of 5.0, 0.8, and 0.4 ppb were measured, leading to daily average doses of 550, 86, and 32 μg/day for Sites 1, 2, and 3 respectively. Average PAN diurnal variation always showed a maximum in the midday, in typical contrast to minimums for virtually all pollutants, at Site 2. This typical diurnal behavior of PAN is shown in Figure 33 for Sites 1, 2, and 3. In all instances, a significant decline is evident toward the evening hours. This can be attributed to the short lifetime of PAN (a few hours), largely a result of its thermal dissociation (Table 9). However, PAN synthesized in late evening is preserved with much smaller loss if cool nights prevail. The PAN maximum at all sites is consistent with its essentially local photochemical source.

Peroxypropionyl Nitrate ($CH_3CH_2COOONO_2$)—Peroxypropionyl nitrate (PPN) is also an organic nitrogen pollutant of secondary origin, formed in a way similar to PAN. This species was found to be less abundant than PAN and was never measured with a frequency of 100 percent at any of the sites. The measurement frequency at Sites 1, 2, and 3 was 86, 47, and 25 percent respectively. Highest PPN levels of 2.5, 0.3, and 0.5 ppb were measured at Sites 1. 2, and 3 respectively. Average concentrations at these sites were 0.7, 0.1, and 0.15 ppb. A clear diurnal variation of PPN existed; its natural identity to PAN is clearly demonstrated in Figure 34.

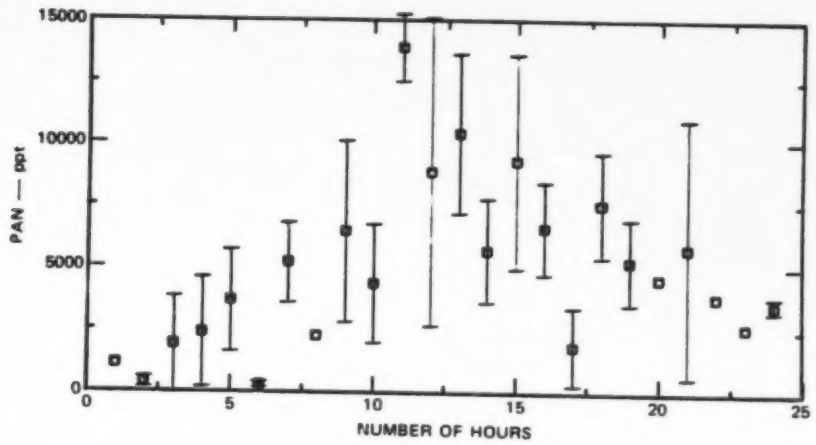


(a) SITE 1 — LOS ANGELES

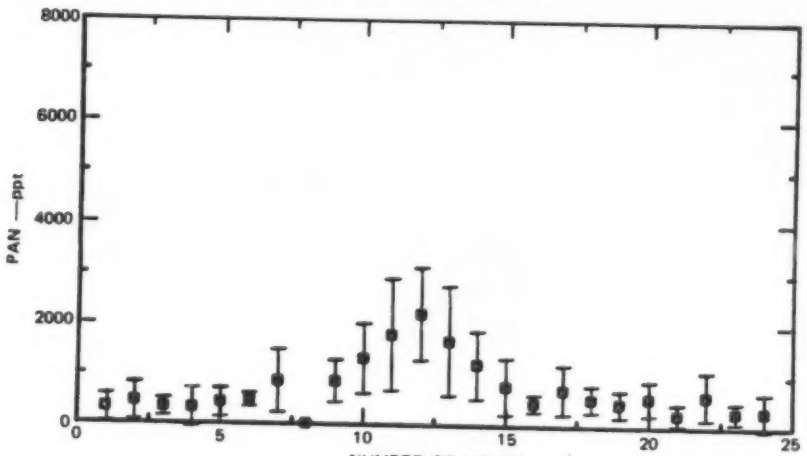


(b) SITE 2 — PHOENIX

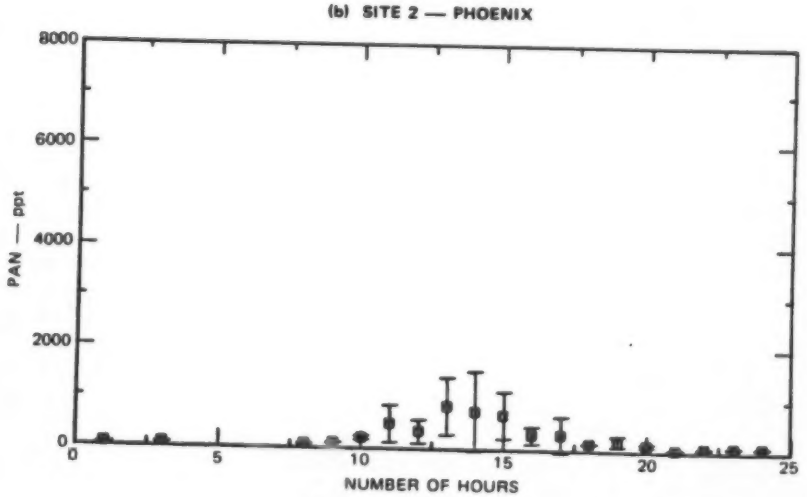
Figure 32. Average diurnal variation of 1,2,4 trimethylbenzene.



(a) SITE 1 — LOS ANGELES



(b) SITE 2 — PHOENIX



(c) SITE 3 — OAKLAND

Figure 33. Average diurnal variation of PAN.

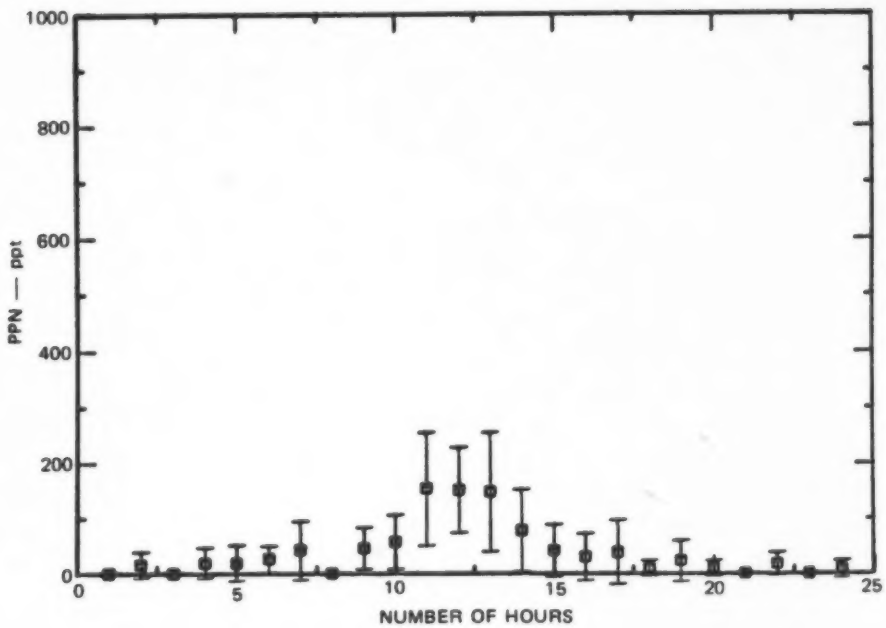


Figure 34. Average diurnal variation of PPN at Phoenix — Site 2.

SECTION 8

FUTURE RESEARCH PLANS

The first year effort of this research project was completed successfully as planned. A great deal of field data for a large number of selected organic chemicals was collected from selected cities. A publication based on this summary report is in preparation.

In the second year a greater emphasis is to be placed on field measurements. The major effort in the second year will be devoted to:

- Expanding the list of toxic chemicals to be measured
- Conducting additional field studies in selected United States cities.

The following cities have been tentatively selected for measurement sites:

- Houston, Texas
- St. Louis, Missouri
- Denver, Colorado
- Riverside, California
- Portland, Oregon.

The measurement program will span several seasons, but attempts will be made to conduct field work during periods when maximum exposure can be expected.

The program of analysis of already-collected field data and the literature search will continue. We shall also continue to develop emissions data bases for those cities where field studies are conducted. An intercalibration program for an exchange of standards is currently being organized by the EPA, and SRI will participate.

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